COMPTES RENDUS
(DOKLADY)
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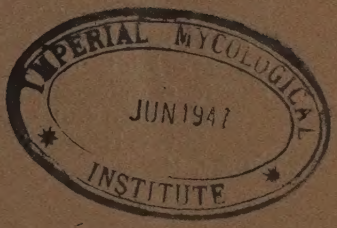
NOUVELLE SÉRIE

1944



VOLUME XLII

№ 4

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1944

VOLUME XLII, № 4

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THEORY OF ELASTICITY

PROPAGATION OF WAVES ON THE SURFACE OF AN INFINITELY LONG CIRCULAR CYLINDER CONCEIVED AS A CUT-OUT PORTION OF AN INFINITELY ELASTIC SPACE

By J. A. MINLDLIN

(Communicated by S. L. Soboleff, Member of the Academy, 8.X.1943)

The present paper is concerned with the simple harmonic motion of plane waves along an infinitely long circular cylinder cut-out within an infinitely elastic space; the surface of the cylinder is supposed to be free from stress. Certain forms of vibrations of an infinitely long circular cylinder have been discussed by Pochhammer (1) and Chree (2). Vibrations of a hollow cylinder have been studied by Ghosh (3).

Let the z-axis be directed along the axis of the cylinder, and denote by r and θ the polar coordinates of the points of a plane perpendicular to the axis of the cylinder.

For simplicity sake we shall confine our discusion to the case of symmetry with respect to z-axis, that is when

$$u_\theta = 0, \quad \frac{\partial u_r}{\partial \theta} = \frac{\partial u_z}{\partial \theta} = 0;$$

u_r, u_θ and u_z are displacements in the direction of the radius, in the direction of θ, and in the direction of the cylinder axis, respectively.

Then the components of the displacement vector may be expressed through the potentials in the well known form

$$u_r = \frac{\partial \varphi}{\partial r} - \frac{\partial \psi}{\partial z}, \quad u_z = \frac{\partial \varphi}{\partial z} + \frac{\partial \psi}{\partial r} + \frac{1}{r}\psi \tag{1}$$

where the functions φ and ψ satisfy the equations:

$$\left.\begin{aligned} \frac{\partial^2 \varphi}{\partial r^2} + \frac{1}{r}\frac{\partial \varphi}{\partial r} + \frac{\partial^2 \varphi}{\partial z^2} &= \frac{1}{a^2}\frac{\partial^2 \varphi}{\partial t^2} \\ \frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r}\frac{\partial \psi}{\partial r} - \frac{1}{r^2}\psi + \frac{\partial^2 \psi}{\partial z^2} &= \frac{1}{b^2}\frac{\partial^2 \psi}{\partial t^2} \end{aligned}\right\} \tag{2}$$

$$a = \sqrt{\frac{\lambda + 2\mu}{\rho}}; \quad b = \sqrt{\frac{\mu}{\rho}}. \tag{3}$$

Here ρ is the density of the medium; λ and μ are the elastic constants of Lamé.

The condition for the absence of stresses on the surface of the cylinder $r = R$ takes the form:

$$\left.\begin{aligned} \widehat{rr}\,\big|_{r=R} &= \left[\frac{\lambda}{r}\frac{\partial (ru_r)}{\partial r} + \lambda\frac{\partial u_z}{\partial z} + 2\mu\frac{\partial u_r}{\partial r}\right]\Big|_{r=R} = 0, \\ \widehat{rz}\,\Big|_{r=R} &= \mu\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)\Big|_{r=R} = 0. \end{aligned}\right\} \tag{4}$$

In accordance with what has been stated above, the solution of equations (2) is sought in the form:

$$\varphi = \varphi_1(r)\, e^{i(pt-\gamma z)}; \quad \psi = \psi_1(r)\, e^{i(pt-\gamma z)}; \quad r \geqslant R. \tag{5}$$

Substituting (5) in (2) we have

$$\left.\begin{aligned} &\frac{d^2\varphi_1}{dr^2} + \frac{1}{r}\frac{d\varphi_1}{dr} - (\gamma^2 - h^2)\varphi_1 = 0 \\ &\frac{d^2\psi_1}{dr^2} + \frac{1}{r}\frac{d\psi_1}{dr} - \left[(\gamma^2 - k^2) + \frac{1}{r^2}\right]\psi_1 = 0 \end{aligned}\right\} \tag{6}$$

$$h^2 = \frac{p^2}{a^2}; \quad k^2 = \frac{p^2}{b^2}. \tag{7}$$

If is natural to consider such perturbations as do not reach deep inside the medium. Then, supposing that $\gamma^2 > k^2$, we take for the integrals of equations (6), MacDonald's functions $K_0(\sqrt{\gamma^2 - h^2}\, r)$ and $K_1(\sqrt{\gamma^2 - k^2}\, r)$ which with $r \to \infty$ are known to tend to zero according to an exponential law.

Thus, the solution of equations (2) under conditions (4) is sought in the form

$$\left.\begin{aligned} \varphi &= AK_0(\sqrt{\gamma^2 - h^2}\, r)\, e^{i(pt-\gamma z)} \\ \psi &= iBK_1(\sqrt{\gamma^2 - k^2}\, r)\, e^{i(pt-\gamma z)} \end{aligned}\right\} \tag{8}$$

where A and B are constants.

From the condition that there are no stresses on the cylinder surface we arrive at the equations

$$2A\gamma\sqrt{\gamma^2 - h^2}\, K_1(\sqrt{\gamma^2 - h^2}\, R) + B(2\gamma^2 - k^2) K_1(\sqrt{\gamma^2 - k^2}\, R) = 0$$

$$A\left[(2\gamma^2 - k^2) K_0(\sqrt{\gamma^2 - h^2}\, R) + \frac{2\sqrt{\gamma^2 - h^2}}{R} K_1(\sqrt{\gamma^2 - h^2} R)\right] +$$

$$+ 2B\gamma\left[(\sqrt{\gamma^2 - k^2}) K_0(\sqrt{\gamma^2 - k^2}\, R) + \frac{1}{R} K_1(\sqrt{\gamma^2 - k^2} R)\right] = 0.$$

After the elimination of the ratio $A : B$, we obtain the condition for the existence of the solutions defined by formula (8). This condition has the form

$$\Phi(\vartheta, \xi) = \left(2\vartheta^2 - \frac{1}{b^2}\right)^2 \frac{K_0\left(\sqrt{\vartheta^2 - \frac{1}{a^2}}\,\frac{1}{\xi}\right)}{K_1\left(\sqrt{\vartheta^2 - \frac{1}{a^2}}\,\frac{1}{\xi}\right)} -$$

$$- 4\vartheta^2\sqrt{\vartheta^2 - \frac{1}{a^2}}\,\sqrt{\vartheta^2 - \frac{1}{b^2}}\,\frac{K_0\left(\sqrt{\vartheta^2 - \frac{1}{b^2}}\,\frac{1}{\xi}\right)}{K_1\left(\sqrt{\vartheta^2 - \frac{1}{b^2}}\,\frac{1}{\xi}\right)} - \frac{2}{b^2}\xi\sqrt{\vartheta^2 - \frac{1}{a^2}} = 0, \tag{9}$$

where $\vartheta = \frac{\gamma}{p}$ denotes a quantity inverse to the velocity of wave motion along the cylinder, and $\xi = \frac{1}{pR}$ is a quantity inverse to the product of the frequency by the radius of the cylinder.

From equation (9) it follows that the wave motion velocity depends upon that product.

Now as we are to investigate the equation (8), let us first establish the monotonous character of the function

$$f(x) = \frac{K_0\left(\frac{1}{x}\right)}{K_1\left(\frac{1}{x}\right)} \tag{10}$$

itself and of its derivative for all but negative values of x. For that purpose we shall use the representations of MacDonald's functions by integrals.

We have for $\xi > 0$

$$K_n(\xi) = \left(\frac{\pi}{2\xi}\right)^{\frac{1}{2}} \frac{e^{-\xi}}{\Gamma\left(n+\frac{1}{2}\right)} \int_0^\infty e^{-z} z^{n-\frac{1}{2}} \left(1+\frac{z}{2\xi}\right)^{n-\frac{1}{2}} dz \quad (n=0, 1). \tag{11}$$

If the numerator and denominator in (10) are substituted with their expressions (11), we get

$$f(x) = \frac{1}{2} \frac{\int_0^\infty e^{-z} z^{-\frac{1}{2}} \left(1+\frac{xz}{2}\right)^{-\frac{1}{2}} dz}{\int_0^\infty e^{-z} z^{\frac{1}{2}} \left(1+\frac{xz}{2}\right)^{\frac{1}{2}} dz}. \tag{12}$$

Upon the differentiation of the two members of equation (12) with respect to x we shall find that

$$f'(x) < 0; \quad \lim_{x\to 0} f'(x) = -\frac{1}{2}. \tag{13}$$

As formula (10) gives $\lim_{x\to 0} f(x) = 1$; $\lim_{x\to\infty} f(x) = 0$, we may conclude from (13) that with x varying from zero to infinity the function $f(x)$ decreases from one to zero, respectively. After twice differentiating both sides of equation (12), we find that $f''(x) > 0$. In order to find the limit of the function $f'(x)$ for $x \to \infty$ we differentiate the two sides of formula (10) and thus obtain $\lim_{x\to\infty} f'(x) = 0$.

In other words, the function $f'(x)$ varies from $-1/2$ to zero, as x increases from zero to infinity.

Denoting for brevity sake

$$h_1 = \sqrt{\vartheta^2 - \frac{1}{a^2}}, \qquad k_1 = \sqrt{\vartheta^2 - \frac{1}{b^2}} \qquad (h_1 > k_1). \tag{14}$$

we can represent the equation (9) in the following form:

$$\Phi(\vartheta, \xi) = \left(2\vartheta^2 - \frac{1}{b^2}\right)^2 f\left(\frac{\xi}{h_1}\right) - 4\vartheta^2 h_1 k_1 f\left(\frac{\xi}{k_1}\right) - \frac{2}{b^2}\xi h_1 = 0. \tag{15}$$

We shall establish the monotonous character of the variation of the function $\Phi(\vartheta, \xi)$ when ξ takes non-negative values and $\vartheta > \frac{1}{b}$ is arbitrarily fixed.

We have

$$\frac{\partial \Phi(\vartheta,\xi)}{\partial \xi}=\frac{1}{h_1}\left\{\left(2\vartheta^2-\frac{1}{b^2}\right)^2 f'\left(\frac{\xi}{h_1}\right)-2h_1^2\left[2\vartheta^2 f'\left(\frac{\xi}{k_1}\right)+\frac{1}{b^2}\right]\right\} \tag{16}$$

or

$$\frac{\partial \Phi(\vartheta,\xi)}{\partial \xi}=\frac{1}{h_1}\left\{4\vartheta^4\left[f'\left(\frac{\xi}{h_1}\right)-f'\left(\frac{\xi}{k_1}\right)\right]+\frac{1}{b^4}f'\left(\frac{\xi}{h_1}\right)-\frac{2\vartheta^2}{b^2}\left[1+2f'\left(\frac{\xi}{h_1}\right)\right]+\right.$$
$$\left.+\frac{2}{a^2}\left[2\vartheta^2 f'\left(\frac{\xi}{k_1}\right)+\frac{1}{b^2}\right]\right\}. \tag{17}$$

As the function $f'(x)$ is an increasing function for all $x\geqslant 0$, it appears that $f'\left(\frac{\xi}{h_1}\right)<f'\left(\frac{\xi}{k_1}\right)$; moreover, $f'(x)<0, |f'(x)|<\frac{1}{2}$.

In virtue of this the first term in formula (16) and the first three terms in (17) are negative quantities.

In case

$$M=2\vartheta^2 f'\left(\frac{\xi}{k_1}\right)+\frac{1}{b^2}\geqslant 0$$

then, according to formula (16),

$$\frac{\partial \Phi(\vartheta,\xi)}{\partial \xi}<0. \tag{18}$$

If, on the other hand, $M\leqslant 0$, the condition (18) follows from formula (17). We have thus proved that $\Phi(\vartheta,\xi)$ considered as a function of ξ is a decreasing function, as ξ varies from zero to infinity, while ϑ is arbitrarily fixed within the interval $\frac{1}{b}<\vartheta<\infty$.

For $\xi=0$ the function $\Phi(\vartheta,\xi)$ is

$$\Phi(\vartheta,0)=F(\vartheta)=\left(2\vartheta^2-\frac{1}{b^2}\right)^2-4\vartheta^2 h_1 k_1.$$

The equation

$$F(\vartheta)=0 \tag{19}$$

is Rayleigh's equation (4) which is known to have but one real positive root in the interval $\frac{1}{b}<\vartheta<\infty$ and a negative root of equal modulus. Let us denote this root by $1/c$. Then for $\xi=0$ the equation (15) has only one real positive root $\vartheta=1/c$, and its other root, equal in modulus to the former, is negative. The derivative $F'(\vartheta)$ is negative for every ϑ lying within the interval $\frac{1}{b}<\vartheta<\infty$. This has been proved by S. Soboleff (5) who had thoroughly investigated the function $F(\vartheta)$.

Thus we have

$$\left(2\vartheta^2-\frac{1}{b^2}\right)^2>4\vartheta^2 h_1 k_1 \qquad \text{for } \vartheta<\frac{1}{c}$$
$$\left(2\vartheta^2-\frac{1}{b^2}\right)^2<4\vartheta^2 h_1 k_1 \qquad \text{for } \vartheta>\frac{1}{c}$$

It is now easy to show the existence of a single real positive root to equation (15) for any fixed ϑ in the interval $\frac{1}{b}<\vartheta<\frac{1}{c}$. Indeed, we have $\Phi(\vartheta,0)>0$; $\Phi(\vartheta,\infty)<0$; $\frac{1}{b}<\vartheta<\frac{1}{c}$. From the formerly established fact that the function $\Phi(\vartheta,\xi)$ is a decreasing function in ξ it follows that equation (15) has a sole real positive root lying in the interval $0<\xi<\infty$ for any ϑ fixed within the interval $\frac{1}{b}<\vartheta<\frac{1}{c}$. Now we shall prove that for any ϑ fixed within the interval $\frac{1}{c}<\vartheta<\infty$ the equation (15) has no real positive roots. In fact, we

have $\Phi(\vartheta, 0) < 0$; $\Phi(\vartheta, \infty) < 0$; $\frac{1}{c} < \vartheta < \infty$, from which our statement follows directly; it remains to show that equation (15) has a single real positive root for $\vartheta = {}^1/_b$.

Substituting in (15) $\vartheta = {}^1/_b$, we get

$$\Phi\left(\frac{1}{b}, \xi\right) = \frac{1}{b^4} f\left(\frac{\xi}{\sqrt{\frac{1}{b^2} - \frac{1}{a^2}}}\right) - \frac{2}{b^2}\xi\sqrt{\frac{1}{b^2} - \frac{1}{a^2}} = 0. \tag{20}$$

The function $\Phi\left(\frac{1}{b}, \xi\right)$ is positive for $\xi = 0$ and negative for ξ infinitely large. That equation (20) has a single real positive root is shown by the fact that the derivative does not change in sign within the interval $0 < \xi < \infty$. It is obvious that in the value $\xi = q$ of the root of the equation (20) we have the upper boundary of the positive real roots of equation (15) for any ϑ from the interval $\frac{1}{b} < \vartheta < \frac{1}{c}$. Remembering that $\xi = \frac{1}{pR}$, where p is frequency, R radius of the cylinder and ϑ the inverse velocity of wave motion along the cylinder, we arrive at the following conclusions.

For a given radius of the cylinder the wave motion along its surface ranges in velocity from the Rayleigh wave to transverse waves. Accordingly, the range of wave-lengths is from 0 to $2\pi qbR$, where q is the root of equation (20), and b the velocity of transverse waves.

In the following communication I will discuss the problem of forced oscillations (Lamb's problem).

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Received
8. X. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

HYDROMECHANICS

FLOW OF OIL TO WELLS IN RESERVOIRS OF CIRCULAR AND BAND-LIKE FORM

By I. A. CHARNY

(Communicated by V. G. Chlopin, Member of the Academy, 1.VI.1943)

By now a series of plane problems have been discussed in the percolation theory, connected with the planning of the position of wells in beds having the form of a half-plane, a band or a circle [1,2].

Below it is shown that in such cases the solution may be obtained in a very simple manner by means of conformal mapping on the basis of the Dupuis formula for a radial flow to a single well located concentrically in a bed of circular shape. This method may as well be used with other forms of beds — oval or crescent, and also when the bed is bounded by faults or pinches out.

What has to be borne in mind while carrying out the mapping is that the radii of the wells change upon transformation in the ratio $\left|\frac{d\zeta}{dz}\right|$; where ζ and z are the planes between which the correspondence $\zeta = \zeta(z)$ is established.

For a single well placed concentrically on the plane ζ_0 in a stratum with a circular contour of feeding, the complex potential has the form

$$W = \Phi + i\psi = \frac{Q}{2\pi} \ln \zeta_0 + \text{const}, \tag{1}$$

where Φ, ψ are the velocity potential and stream function, respectively; $\Phi = \frac{kp}{\mu}$; k is permeability of the medium; μ, absolute viscosity of the fluid; p, pressure; Q, the production of the well per a unit thickness of the stratum. If the values of the potential on the contour of the well $r = \rho_0$ and on that of the stratum $r = \rho_k$ are Φ_c and Φ_k, respectively, we have

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln \frac{\rho_k}{\rho_0}}. \tag{2}$$

This is the equation we shall proceed upon. Now let us consider some examples.

1. Flow to a well placed excentrically in a stratum of circular outline (Fig. 1,*a*). Put

$$\zeta_0 = \frac{\zeta + \delta}{1 + \frac{\delta\zeta}{\rho_k^2}}. \tag{3}$$

Obviously, $\zeta_0 = 0$ if $\zeta = -\delta$, and $|\zeta_0| = \rho_k$ if $\zeta_0 = \rho_k$. Further, we have

$$\left|\frac{d\zeta_0}{d\zeta}\right|_{\zeta=-\delta} = \frac{1}{1-\frac{\delta^2}{\rho_k^2}}$$

whence

$$\rho_e = \frac{\rho_k}{1-\frac{\delta^2}{\rho_k^2}}. \tag{4}$$

Assuming the contour conditions of the planes ζ_0 and ζ to be equal, we find ultimately from (1) and (2) that

$$W = \frac{Q}{2\pi} \ln \frac{\zeta+\delta}{1+\frac{\delta\zeta}{\rho_k^2}} + C \tag{5}$$

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln \frac{\rho_k}{\rho_c}\left(1-\frac{\delta^2}{\rho_k^2}\right)}. \tag{6}$$

From this the production of a single well in a stratum of rectilinear feeding contour may easily be obtained (Fig. 1, *b*). Setting $\delta = \rho_k - H$, we derive

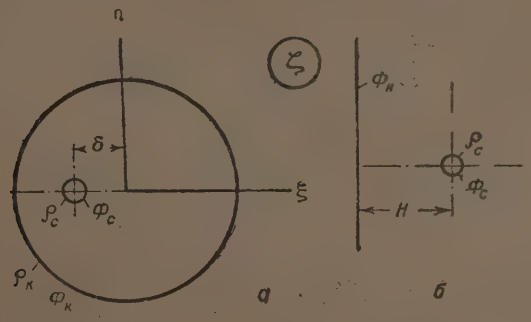

Fig. 1

from (6)

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln \frac{\rho_k}{\rho_c}\left(1-\frac{\delta^2}{\rho_k^2}\right)} = \frac{2\pi(\Phi_k - \Phi_c)}{\ln \frac{(2\rho_k - H)H}{\rho_c \rho_k}}.$$

Hence for $\rho_k \to \infty$ we have

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln \frac{2H}{\rho_c}}. \tag{7}$$

2. Flow to arbitrarily arranged wells in a circular stratum (n, number of wells). After the rotation of the coordinate axes we obtain from (5), by making use of the superposition principle,

$$W = \frac{1}{2\pi} \sum_{i=1}^{n} Q_i \ln \frac{ze^{-i\alpha_i} - \delta_i}{1 - \frac{z\delta_i e^{-i\alpha_i}}{R_k^2}} + C \tag{8}$$

where δ_i, α_i are polar coordinates of the centre of the i-th well.

From (8) after the real part is separated, we find the expression for the potential at any point of the stratum:

$$\Phi = \frac{1}{4\pi}\sum_{i=1}^{n} Q_i \ln R_k^2 \frac{r^2 + \delta_i^2 - 2r\delta_i \cos(\theta - \alpha_i)}{R_k^2 + \frac{r^2\delta_i^2}{R_k^2} - 2r\delta_i \cos(\theta - \alpha_i)} + C. \tag{9}$$

The production rates Q_i and C are determined from the known values Φ_c and Φ_k on the contours of the wells and on that of the stratum, respectively. As the radii of the wells r_c are negligibly small in comparison with the

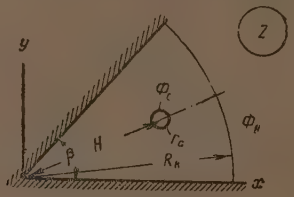

Fig. 2

distances δ_i, the following system for Q_i and C may be obtained from (9) and (6):

$$\Phi_{jc} = \frac{1}{4\pi}\sum_{i=1}^{n}{}' Q_i \ln R_k^2 \frac{\delta_j^2 + \delta_i^2 - 2\delta_i\delta_j \cos(\alpha_i - \alpha_j)}{R_k^2 + \frac{\delta_i^2\delta_j^2}{R_k^2} - 2\delta_i\delta_j \cos(\alpha_i - \alpha_j)} +$$

$$+ \frac{Q_j}{2\pi} \ln \frac{r_{jc}}{1 - \frac{\delta_j^2}{R_k^2}} + C \quad (j = 1, 2, 3, \ldots, n) \tag{10}$$

$$\Phi_k = \frac{1}{2\pi} \ln R_k \sum_{i=1}^{n} Q_i + C. \tag{11}$$

The apostroph signifies as usual that on summation from $i = 1$ to $i = n$ the term $i = j$ is omitted.

3. Flow to a well located on the axis of a stratum pinching out at a given angle (Fig. 2). We shall proceed from a flow to an excentrical well (Fig. 1), the axis $o\xi$ for this flow being a streamline. In that case the plane of the flow (Fig. 1) can be imagined to be cut up along the positive axis $o\xi$, and then the transformation

$$\zeta = z^{\varkappa}, \qquad \varkappa = \frac{2\pi}{\beta} \tag{12}$$

converts the flow of Fig. 1 into the one of Fig. 2. In determining the production rate we use the formula (6) in which ρ_k, δ and ρ_c must be substituted with $R_k^{\varkappa}$, $H^{\varkappa}$ and $r_c \left|\frac{d\zeta}{dz}\right|_{z=He^{i\beta/2}} = r_c \varkappa H^{\varkappa-1}$, respectively. Then

$$Q = 2\pi \frac{\Phi_k - \Phi_c}{\ln \frac{R_k^{\varkappa}}{\varkappa r_c H^{\varkappa-1}\left(1 - \frac{H^{2\varkappa}}{R_k^{2\varkappa}}\right)}}. \tag{13}$$

It may be noted that if $\varkappa = m$ is an integer, the formula (13) simultaneously gives the production rate of a battery of wells set symmetrically on a circle

under equal conditions. To derive for $\varkappa = m$ the formulae (6) and (13) for equal conditions is usually a more complicated and lengthy operation ([1],[2]).

4. Flow to an infinite array of wells situated under equal conditions in a stratum with a linear feeding contour (Fig. 3). Proceeding from the flow of Fig. 1 and formula (6), we put

$$\zeta = \rho_k e^{i\frac{2\pi z}{a}}. \tag{14}$$

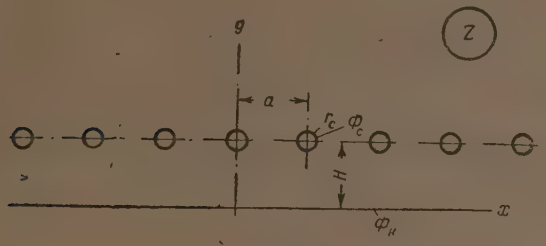

Fig. 3

Then a well of the plane ζ converts into an infinite array of wells in the plane z with distance a between one well and the next. Further,

$$\delta = \rho_k e^{-\frac{2\pi H}{a}}; \qquad \left|\frac{d\zeta}{dz}\right|_{\substack{z=iH+na \\ n=1,2,\ldots}} = \frac{2\pi}{a}\rho_k e^{-\frac{2\pi H}{a}}; \qquad \rho_c = r_c\frac{2\pi\rho_k}{a}e^{-\frac{2\pi H}{a}}. \tag{15}$$

Then from (6)

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln\frac{a}{\pi r_c}\operatorname{sh}\frac{2\pi H}{a}}. \tag{16}$$

Muskat in solving this problem has made a much longer way to obtain

$$Q = \frac{2\pi(\Phi_k - \Phi_c)}{\ln\frac{\operatorname{sh}\frac{2\pi H}{a}}{\operatorname{sh}\frac{\pi r_c}{a}}} \tag{16'}$$

As r_c is small in comparison with a, the formulae (16) and (16′) practically coincide.

Received
1. VI. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PHYSIQUE MATHÉMATIQUE

SUR LES CONDITIONS NÉCESSAIRES ET SUFFISANTES POUR L'EXISTENCE D'UN CENTRE

Par I. S. KOUKLESS

(Présenté par S. L. Soboleff, de l'Académie, le 24.X.1943.)

Théorème. *Pour que l'origine soit un centre pour l'équation*

$$\frac{dy}{dx} = \frac{-x + F(x, y)}{y} \tag{1}$$

(*F étant une fonction analytique ne contenant pas de termes linéaires*), *il faut et il suffit que l'on ait:* $\Phi(\alpha, \beta)$ *étant une fonction donnée analytique, pour* α *et* β *assez petits, et d'ailleurs quelconque, il existe une fonction* $v(x, y)$ *analytique au voisinage de l'origine et vérifiant dans ce voisinage les conditions:* a) $\frac{dv}{dy}(0, 0) = 0$; b) $\frac{d^2v}{dy^2}(0, 0) = 1$; c) $\frac{d^{2n}v}{dx^{2n}}(0, 0) = 0$ $(n = 2, 3, 4 \ldots)$ *et telle que l'on a l'identité*

$$-x + F(x, y) = y \frac{\Phi(x, v) - \frac{dv}{dx}}{\frac{dv}{dy}}. \tag{2}$$

D'ailleurs, si $\Phi(x, v)$ est donnée et si l'origine est un centre pour l'équation (1) considérée, la fonction $v(x, y)$ est déterminée d'une manière unique (1). En posant

$$\Phi = \sum_{i=0}^{\infty} \left(\frac{1}{2} \lambda_0^{(i)} y^2 + \frac{1}{3} \lambda_1^{(i)} y^2 + \ldots + \frac{1}{n} \lambda_n^{(i)} y^n + \ldots \right) x^i$$

et

$$-x + F(x, y) = \sum_{i=0}^{\infty} (a_0 + a_1^i y + a_2^i y^2 + \ldots + a_n^i y^n + \ldots) x^i,$$

$$\lambda_0^{(0)} = 1, \quad a_0^{(0)} = a_1^{(0)} = 0 \quad \text{et} \quad a_0^{(1)} = -1$$

et en tenant compte de l'identité (2), on obtient une infinité d'équations linéaires contenant les coefficients inconnus $\lambda_i^{(j)}$ de la fonction Φ et les coefficients connus $a_k^{(i)}$.

La première de ces équations est de la forme $a_2^{(0)} + \frac{1}{2}\lambda_1^{(0)}] = 0$, c'est-à-dire c'est une équation avec une seule inconnue $\lambda_1^{(0)}$. La seconde équation est de la forme $a_3^{(0)} + \lambda_1^{(0)} a_2^{(0)} + \frac{1}{3}\lambda_1^{(1)} = 0$, c'est-à-dire elle contient une inconnue de plus que la première. On peut montrer que toutes les équations de notre système infini peuvent être disposées dans un tel ordre qu'avec chaque nouvelle équation il apparaît une et une seule nouvelle inconnue de la forme $\lambda_i^{(j)}$, et d'ailleurs cette nouvelle inconnue a un coefficient non nul. D'ailleurs, le terme $\lambda_2^{(0)}$ intervient pour la première fois dans la 4-ième équation, le membre $\lambda_1^{(0)}$ dans la 12-ième équation et, en général, le membre de la forme $\lambda_{2n}^{(0)}$ intervient pour la première fois dans la $2n(n+1)$ équation $(n = 1, 2, 3, \ldots)$.

En sachant que tous les termes de la forme $\lambda_{2n}^{(0)}$ doivent être nuls, on conclut en vertu de la condition b) de notre théorème que pour que notre système d'équations soit compatible, il faut que dans le système infini des déterminants d'ordre $2n(n+1)$ $(n = 1, 2, 3, \ldots)$ tous les déterminants soient nuls.

Il est démontré que chacun des déterminants d'ordre $2n(n+1)$ de cette nature présente le n-ième indice du foyer (n-te Strudelgrösse), donc nous avons ainsi la possibilité d'écrire directement les conditions nécessaires et suffisantes pour un centre et les présenter sous forme explicite [au lieu de considérer des relations de récurrence ainsi que l'ont fait Bendixon (2) et Frommer (3)], parce que nos déterminants (c'est-à-dire les valeurs successives des foyers) ne contiennent pas d'éléments inconnus. Le n-ième indice du foyer présente un déterminant d'ordre $2n(n+1)$ qui est formé de la manière suivante.

Considérons un groupe de $4n+4$ symboles verticaux de la forme $\left(\frac{p}{q}\right)$, tels que chaque symbole suivant est écrit au-dessus du précédent, et d'ailleurs divisons ce groupe en 4 sections.

La première section contient n symboles de la forme

$$\left(\frac{2k+1}{2n-2k}\right) \quad (k = 0, 1, 2, \ldots, n-1).$$

La seconde section contient $n+1$ symboles de la forme

$$\left(\frac{2k}{2n+2+2k}\right) \quad (k = 0, 1, 2, \ldots, n).$$

La troisième section contient $n+1$ symboles de la forme

$$\left(\frac{2n+1-2k}{2k+1}\right) \quad (k = 0, 1, 2, \ldots, n),$$

et enfin la quatrième section contient $n+2$ symboles de la forme

$$\left(\frac{2k}{2n+3-2k}\right) \quad (k = 0, 1, 2, \ldots, n+1).$$

Toutes ces quatre sections de symboles écrites successivement l'une au-dessous de l'autre seront nommées n-ième groupe de symboles verticaux.

Ainsi nous aurons le groupe nul de symboles (pour $n = 0$) contenant seulement 4 symboles, le premier groupe (pour $n = 1$) contenant 12 symboles, le second groupe, etc. Formons le groupe de $4n+4$ symboles horizontaux de la forme $\left(\frac{r}{s}\right)$ écrits successivement l'un à droite de l'autre, et d'ailleurs, d'une manière analogue aux symboles verticaux, divisons ce groupe en quatre sections.

Dans la première section nous aurons $n+1$ symboles de la forme $\left(\frac{2k}{2n-2k}\right)$, dans la seconde section $n+1$ symboles de la forme $\left(\frac{1+2k}{2n-2k}\right)$,

dans la troisième section $n+1$ symboles de la forme $\left(\frac{2n-2k}{1+2k}\right)$ et dans la quatrième section $n+1$ symboles de la forme $\left(\frac{2k+1}{2n+1-2k}\right)$.

Dans toutes les quatre sections k parcourt les valeurs de 0 jusqu'à n. Tous ces $4n+4$ symboles seront nommés n-ième groupe de symboles horizontaux. Pour écrire le déterminant D_p (c'est-à-dire le p-ième indice du foyer), prenons un carré et divisons chacun de ses côtés en $2p(p+1)$ parties égales, parce que l'ordre de notre déterminant est égal à $2p(p+1)$. Au-dessus du carré écrivons les symboles horizontaux de sorte qu'à chaque colonne du déterminant il corresponde un symbole horizontal, et à gauche du carré écrivons les symboles verticaux de sorte qu'à chaque ligne du déterminant il corresponde un symbole vertical.

D'ailleurs, les symboles eux-mêmes sont situés ainsi: écrivons d'abord le groupe nul des symboles horizontaux, ensuite le premier, second,, etc. et enfin le $p-1$-ième groupe de ces symboles, en écrivant chaque groupe suivant à droite du précédent. Le schème qui suit représente quatre groupes consécutifs de symboles horizontaux.

Ainsi nous avons en tout $4+8+\ldots 4p=2p(p+1)$ symboles horizontaux, c'est-à-dire autant que le nombre de colonnes dans notre déterminant; donc, si l'on écrit au-dessus de la première colonne (en comptant de gauche à droite) le premier symbole horizontal, le dernier de ces symboles sera écrit au-dessus de la dernière colonne.

D'une manière analogue on dispose les symboles verticaux à droite de notre déterminant: d'abord on écrit le groupe nul, ensuite le premier, le second, etc., et enfin le $(p-1)$-ième; on inscrit ces groupes successivement l'un au-dessous de l'autre de sorte qu'à chaque ligne du déterminant il corresponde un symbole vertical. Dès que tous les symboles verticaux et horizontaux sont écrits, il n'y a aucune difficulté à former le déterminant lui-même: l'élément qui se trouve dans la ligne ayant pour symbole $\left(\frac{r}{s}\right)$ et dans la colonne ayant le symbole $\frac{p}{q}$ est de la forme $a_{s-q}^{(r-p)}$; c'est-à-dire en soustrayant de l'indice supérieur du symbole vertical l'indice supérieur du symbole horizontal et de l'indice inférieur du symbole vertical l'indice inférieur du symbole horizontal, on aura respectivement les indices supérieur et inférieur de l'élément correspondant a_i^j du déterminant. D'ailleurs, si un indice quelconque d'un élément a_i^j devient négatif, il faut considérer cet élément comme nul, et d'ailleurs il faut se rappeler que $a_1^{(0)}=a_0^{(}=0$ et $a_0^{(1)}=-1$.

Dans la règle que nous venons de donner il y a deux exceptions: 1) les éléments dont les symboles horizontaux ont la forme $\left(\frac{r}{s}\right)$ et les éléments verticaux la forme $\left(\frac{r+1}{s-2}\right)$ sont égaux aux fractions $\frac{r+1}{s}$, et 2) les éléments ayant les symboles horizontaux de la forme $\left(\frac{2k}{1}\right)$ et les symboles verticaux de la forme $\frac{0}{2k}$ $(k=1, 2, 3, \ldots)$ nous prendrons égaux à 1.

En supposant que la fonction $-x+F(x, y)$ présente un polynôme du 3-ième degré, nous représentons ici le «premier indice du foyer», formé suivant la règle précédente (nous le plaçons à l'intérieur du carré $ABB'B''$), le second (à l'intérieur du carré $ACC'C''$), le troisième (à l'intérieur du carré $ADD'D''$), le quatrième (à l'intérieur du carré $AEE'E''$), le cinquième (à l'intérieur du carré $AFF'F''$) (voir le schème).

Nous voyons que le schème de chaque indice du foyer contient les schèmes de tous les indices précédents du foyer.

On peut montrer que les cinq indices du foyer représentés sur le schème que nous donnons ici, ne peuvent s'annuler simultanément que dans les quatre cas suivants:

$$
\begin{aligned}
1)\ \alpha &= a_0^{(3)} a_1^{(1)2} + a_1^{(2)}(a_2^{(0)} a_1^{(1)} + 3a_3^{(0)}) = 0;\\
\delta &= [3a_3^{(0)}\ (a_2^{(0)} a_1^{(1)} + 3a_2^{(0)}) + (a_2^{(0)} a_1^{(1)} + 3a_3^{(0)})^2 +\\
&\quad + a_2^{(1)} a_1^{(1)2}]\, a_1^{(2)} - 3a_3^{(0)}\,(a_2^{(0)} a_1^{(1)} + 3a_3^{(0)})^3 -\\
&\quad - a_2^{(1)}\, a_1^{(1)2}\,(a_2^{(0)} a_1^{(1)} + 3a_3^{(0)}) = 0;\\
\varkappa &= (a_2^{(0)} + a_0^{(2)})\, a_1^{(1)} + a_1^{(2)} + 3a_3^{(0)} = 0;\\
\tau &= 9a_2^{(1)} a_1^{(1)2} + 2a_1^{(1)4} + 9\,(a_2^{(0)} a_1^{(1)} + 3a_3^{(0)})^2 +\\
&\quad + 27a_3^{(0)}\ (a_2^{(0)} a_1^{(1)} + 3a_3^{(0)}) = 0;
\end{aligned}
$$

$$2)\ a_3^{(0)} = \alpha = \delta = \varkappa = 0;$$

$$3)\ a_2^{(0)} = a_1^{(1)} = a_1^{(2)} = 0;$$

$$4)\ a_3^{(0)} = a_2^{(0)} = a^{(2)} = a_1^{(2)} = 0.$$

On peut montrer que dans chacun des quatre cas décrits tous les indices du foyer s'annulent simultanément, donc l'origine est un centre.

Manuscrit reçu
le 20. XI. 1943.

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* Je profite de l'occasion pour corriger les fautes suivantes qui se sont glissées dans la Note [1]: 1) Dans le texte russe de cette Note le numérateur du second membre de la formule (8) est, par erreur, suivi des points de suspension. 2) Dans les textes russe et français j'ai laissé passé la phrase suivante se rapportant à l'exemple (6): «nous supposons que $h=af=0$».

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PHYSICS

POLARIZATION OF LIGHT SCATTERED BY EXCITED ATOMS

By V. HERMAN

(Communicated by S. I. Wawilow, Member of the Academy, 3.VII.1943)

In the case of ordinary scattering the polarization properties of light are known to be defined by Placzek's formulae (1) which have been derived from Heisenberg—Cramers' (1,2) formula for intensities. These formulae cannot, however, be applied in the case of light scattered by excited atoms.

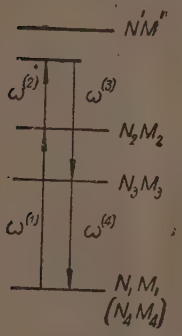

Fig. 1

Weisskopf (3,4) was the first to show their inapplicability to be due to the fact that the lifetime of an atom in the excited state cannot possibly be considered infinitely great in comparison with intermediate states. In this connexion the scattering proper and the excitation of an atom can no longer be treated as separate processes, just as we cannot separate the absorption and emission of a photon in discussing the process of ordinary scattering. The present note is concerned with polarization of light scattered by excited atoms. As a starting point of our discussion we shall take Weisskopf's (3) expression for the intensity of light scattered by excited atoms, which is a different case from ordinary scattering by unexcited atoms, investigated by Placzek (1,3), who took as point of departure Heisenberg—Cramers' formula.

If excitation is due to light, scattering by excited atoms should be regarded as a single process involving four quanta, which begins and ends at the ground or metastable level, and comprises along with the two-quantum act of direct scattering, also the processes of excitation and return of the atom to stable state.

It is because the process considered involves four quanta that Weisskopf's formula (3) obtained accordingly in fourth approximation differs in structure from that of Heisenberg—Cramers, which, corresponding to a process involving two atoms, is obtained in second approximation. And so in the former we find the intensity (see below) to be determined by squared moduli of expressions representing, according to their tensor properties, components of a tensor of the 4th rank and not of the second rank, as is necessarily the case in the Heisenberg—Cramers formula.

Accordingly, the ensuing polarization properties of scattered light will also be different. This after all is made obvious qualitatively by the fact that, for excited atoms, along with polarization of the light that undergoes scattering, an essential part is also played by polarization of the light responsible for excitation.

It may be remarked that discussion from this angle makes it possible, moreover, strictly to determine the polarization of the so-called «step-radiation». Let $\omega^{(1)}$, $\mathbf{l}^{(1)}$, $\mathbf{n}^{(1)}$ be frequency, polarization and direction of the propagation of

a photon which transfers the atom from its ground state N_1, M_1 to the excited one N_2, M_2 (where M_1, M_2 are the magnetic, and N_1, N_2 all the other quantum numbers of these states). At this excited level the act of scattering takes place: the photon $\omega^{(2)}$; $\mathbf{l}^{(2)}$, $\mathbf{n}^{(2)}$ of the incident light (scattering) is absorbed, the photon $\omega^{(3)}$; $\mathbf{l}^{(3)}$; $\mathbf{n}^{(3)}$ is emitted (scattered photon). This is attended by the transition of the atom into the final excited state N_3, M_3. Lastly, upon transition from the state N_3 M_3 to the ground (or metastable) state N_4, M_4, photon $\omega^{(4)}$, $\mathbf{l}^{(4)}$, $\mathbf{n}^{(4)}$ is emitted.

If we omit the constant factor depending on the frequencies $\omega_{N_2N_1} \sim \omega^{(1)}$, $\omega_{N_3N_1} \sim \omega^{(4)}$ which is of no import here, then the probability of such four-quantum process $W_{N_4}^{N_1}$ is equal to[3]

$$W_{N_4}^{N_1} = \frac{1}{2I_1+1} \sum_{M_1, M_4} W_{N_4M_4}^{N_1M_1} \simeq \frac{4}{2I_1+1} \sum_{M_1, M_4} \left| \{f_{iklm}\}_{N_4M_4}^{N_1M_1} l_i^{(1)} l_k^{(2)} l_l^{(3)} l_m^{(4)} \right|^2$$

where $\{f_{iklm}\}_{N_4M_4}^{N_1M_1}$ stands for the following expression of the matrix elements $(P_i)_{N_2M_2}^{N_1M_1}$ and the components of the polarizability tensor $(C_{kl})_{N_3M_3}^{N_2M_2}$:

$$\{f_{iklm}\}_{N_4M_4}^{N_1M_1} = \sum_{M_2, M_3} (P_i)_{N_2M_2}^{N_1M_1} (C_{kl})_{N_3M_3}^{N_2M_2} (P_m)_{N_4M_4}^{N_3M_3} (i, k, l, m = 1, 2, 3),$$

$$(C_{kl})_{N_3M_3}^{N_2M_2} = \sum_{N', M'} \left(\frac{(P_k)_{N'M'}^{N_2M_2} (P_l)_{N_3M_3}^{N'M'}}{\omega_{N'N_1} - \omega^{(1)} - \omega^{(2)} + i\Gamma^{N'}} + \frac{(P_l)_{N'M'}^{N_3M_2} (P_k)_{N_3M_3}^{N'M'}}{\omega_{N'N_1} - \omega^{(1)} + \omega^{(3)} + i\Gamma^{N'}} \right).$$

From the expression given above for $W_{N_4}^{N_1}$ it may be seen that the polarizations $l_i^{(1)}$, $l_k^{(2)}$, $l_l^{(3)}$, $l_m^{(4)}$ enter in the form of various combinations of scalar products with matrix elements of the dipole moment. Because of the presence of the well known rules of selection for M determined by the tensor properties of the matrix element f_{iklm}, these will essentially affect the dependence of $W_{N_4}^{N_1}$ upon polarization. In order to obtain the polarization formulae we are interested in, i. e. for defining the dependence on polarizations in an explicit form, it is necessary to carry out the summation over magnetic quantum numbers. The double sum $\sum_{M_1, M_4}$ can be reduced ([5,6]) to a single summation followed by three-dimensional averaging. We also take the average over the polarizations $\mathbf{l}^{(4)}$ and over the direction $\mathbf{n}^{(4)}$ in which the photon is emitted when the atom returns to its initial state. Their influence is of no interest to us. The tensor entering in $W_{N_4}^{N_1}$ is then lowered in rank by two units $\left[\text{because } \overline{l_m^{(4)} l_l^{(4)}} = \frac{1}{2} \left(\delta_{ml} - \overline{n_m^{(4)} n_l^{(4)}} \right) = \frac{1}{3} \delta_{ml} \right]$ and we arrive at the following expression:

$$W_{N_4}^{N_1} = \sum_{M_4'} (f_{iklm})_{N_1M_4}^{N_10} (f^*_{pqsn})_{N_1M_4'}^{N_10} l_i^{(1)} l_k^{(2)} l_l^{(3)} l_n^{(1)} l_p^{(2)} l_r^{(3)}.$$

The components of the tensor of rank 6 entering into this expression lend themselves easily to three-dimensional averaging by the method indicated in ([6]).

Let us now determine, in some concrete cases, the degrees of depolarization of scattered light as related to the polarization $\mathbf{l}^{(1)}$ of the exciting light and the polarization $\mathbf{l}^{(2)}$ of the light subject to scattering. Let us introduce a Cartesian system of coordinates with unit vectors $\mathbf{i}_1$, $\mathbf{i}_2$, $\mathbf{i}_3$ (Fig. 2). The unit vector $\mathbf{i}_3$ is defined to have the same direction with the propagation of the light responsible for the excitation of the atom $\mathbf{n}^{(1)}$; $\mathbf{i}_2$ is placed in the plane $\mathbf{n}^{(1)}$, $\mathbf{n}^{(2)}$. We

make use of yet another orthogonal system of unit vectors $\mathbf{n}^{(2)}$, $\vartheta^{(2)}$, $\varphi^{(2)}$ connected with $\mathbf{n}^{(2)}$ and having $\vartheta^{(2)}$ lying in the plane $\mathbf{n}^{(1)}, \mathbf{n}^{(2)}$. Correspondingly, we tie up the unit vectors $\vartheta^{(3)}$ (in the plane $\mathbf{n}^{(1)}, \mathbf{n}^{(3)}$) and $\varphi^{(3)}$ ($\perp$ to that plane) to the direction of the scattered light $\mathbf{n}^{(3)}$. The angle between $\mathbf{n}^{(1)}$ and $\mathbf{n}^{(3)}$ we denote by θ_{13}, and that between $\mathbf{n}^{(1)}$ and $\mathbf{n}^{(2)}$, by θ_{12}. The angle between the planes $\mathbf{n}^{(1)}$, $\mathbf{n}^{(2)}$ and $\mathbf{n}^{(1)}$, $\mathbf{n}^{(3)}$ will be denoted by Φ. Let the exciting light be linearly polarized along $\mathbf{i}_1$ ($\mathbf{l}^{(1)} = \mathbf{i}^{(1)}$), while the light subject to scattering is assumed to be polarized along $\varphi^{(2)}$ ($\mathbf{l}^{(2)} = \varphi^{(2)} = -\mathbf{i}_1$).

The coefficient of depolarization of the scattered light will be understood to mean what it usually does — the ratio of probabilities, or their proportional

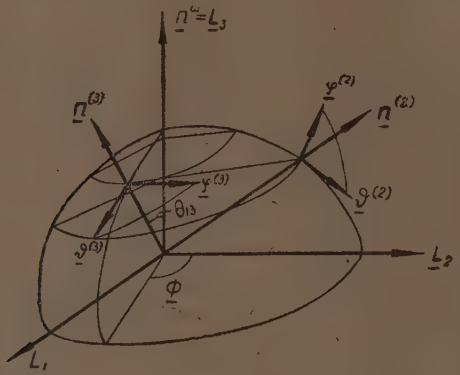

Fig. 2

intensities of the scattered light with polarization $\mathbf{l}^{(3)}$ perpendicular to the plane $\mathbf{n}^{(1)}$, $\mathbf{n}^{(3)}$ to the intensity with polarization $\mathbf{l}^{(3)}$ parallel to the plane $\mathbf{n}^{(1)}$, $\mathbf{n}^{(3)}$, i. e. $\mathbf{l}^{(3)} = \left\{ \begin{matrix} \varphi^{(3)} \\ \vartheta^{(3)} \end{matrix} \right\}$.

Substitution in $W_{N_4}^{N_1}$ leads after averaging by the method suggested in [6] to the following result:

$$\rho_{\perp,\parallel}^{\perp,\perp} \equiv \frac{I(\mathbf{l}^{(2)} \perp \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(2)};\ \mathbf{l}^{(3)} \perp \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(3)})}{I(\mathbf{l}^{(2)} \perp \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(2)};\ \mathbf{l}^{(3)} \parallel \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(3)})} = \frac{\frac{2\rho_0 - 1}{2\rho_0 + 1}(3\cos^2\varphi - 1) + \sin^2\Phi}{\frac{2\rho_0 - 1}{2\rho_0 + 1}(3\cos^2\theta_{13}\sin^2\Phi - 1) + (1 - \cos^2\theta_{13}\sin^2\Phi)} \tag{1}$$

where ρ_0 is the value of the depolarization coefficient for $\theta_{13} = \frac{\pi}{2}$, $\Phi = \frac{\pi}{4}$. We have introduced it in order to eliminate the invariants f_{iklm} upon which the result of averaging depends. Here, as in other cases of the dispersion theory, the direct computation of invariants may hardly be effected in practice, except the tedious computations for the hydrogen atom which are of no interest in our case. A similar reasoning in determining depolarization can be applied in any other case.

If, for instance, $\mathbf{l}^{(1)} = \mathbf{i}_1$, we shall find that

$$\rho_{\perp,\parallel}^{\perp,\perp} \equiv \frac{I(\mathbf{l}^{(2)} \perp \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(2)};\ \mathbf{l}^{(3)} \perp \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(3)})}{I(\mathbf{l}^{(2)} \parallel \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(2)};\ \mathbf{l}^{(3)} \parallel \text{pl. } \mathbf{n}^{(1)}, \mathbf{n}^{(3)})} = (\rho_{\frac{\pi}{4}} - 1)\cos^2\Phi + \sin^2\Phi \tag{2}$$

where $\rho_{\frac{\pi}{4}} = \rho_{\perp,\parallel}^{\perp,\perp}\left(\Phi = \frac{\pi}{4}\right)$.

For characterizing the polarization properties of the scattered light, it is essential also to know the inversion coefficient P, by which is meant, in the case of a right-hand polarized incident light, the ratio of the intensity of a regularly, that is also dextrally polarized light, to the intensity of scattering with inverted, or left-hand polarization. It will be obvious that in the case of scattering by excited atoms, which is just considered by us, the inversion coefficient P will, generally speaking, depend upon the polarization of the light responsible for excitation.

I will here confine myself to referring to that single case when the excitation is caused by a right-hand polarized light, while the light that undergoes scattering shows left-hand polarization. In this case the result is analogous to Placzek's formula ([1]). A similar expression is obtained if the light responsible for excitation is not polarized at all, and the light undergoing scattering is dextrally polarized. This accounts for the fact that the result observed in this case coincides with the formula of Placzek except for the difference in the value of P_0:

$$P = \frac{4\sin^2\frac{\theta_{23}}{2} + (13 + 10\cos\theta_{23} + \cos^2\theta_{23})\frac{P_0}{6-P_0}}{4\cos^2\frac{\theta_{23}}{2} + (13 - 10\cos\theta_{23})\frac{P_0}{6-P_0}} \qquad (3)$$

where P_0 is the value of the inversion coefficient for $\theta_{23} = 0$.

It may be remarked in conclusion that a similar treatment of the polarization of scattered light is possible with a different method of excitation, in the case of electron shock, for instance ([7]). In that case which will not be discussed here, ρ and P are determined by the direction of the impulse of the electron beam (or, strictly speaking, by the average impulse change on collision) responsible for excitation, and by the direction of the scattered light polarization.

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Received
5. VI. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PHYSICS

ON THE SCATTERING OF LIGHT IN LIQUIDS

By V. L. GINSBURG

(Communicated by S. I. Wawilow, Member of the Academy, 2.VII. 1943)

A series of articles were recently published on the scattering of light in liquids [1]*. These papers contain considerable experimental material, but the discussion of the question and the comparison of the experimental data with the theory cannot be considered satisfactory. The present paper is devoted to a discussion of several of the results and assertions made in [1].

The intensity of light scattered in fluctuations of density is distributed between the undisplaced line and the Mandelstamm-Brillouin doublet. The ratio of the intensity of the central line to the total intensity of the doublet components equals [2]

$$\frac{I_c}{I_d} = \frac{C_p - C_v}{C_v}. \qquad (1)$$

Formula (1) refers to the integral intensity. Both the components of the doublet and the central line have a finite width, connected with the decay of the density fluctuations in time, the intensity distribution near the centre of each line having a dispersive character:

$$I(\Omega) = \frac{I\,\delta/\pi}{\Omega^2 + \delta^2},$$

where Ω is the cyclic frequency measured from the centre of the line; δ, the half-width $I(\delta) = \frac{I(0)}{2}$, and the coefficient is so chosen that $\int_{-\infty}^{+\infty} I(\Omega)\, d\Omega = I$. The width of the central line is determined by the heat conductivity and $\delta_c = \left(\frac{2\pi}{\Lambda}\right)^2 \nu$, where ν is the coefficient of heat conductivity and $\Lambda = \frac{\lambda}{2 \sin \frac{\varphi}{2}}$ (λ is the wave-length of light in the liquid; φ, the scattering angle). The width of the doublet lines is connected with the damping coefficient of the sound of wave-length Λ and equals

$$\delta_d = \alpha a = \left(\frac{2\pi}{\Lambda}\right)^2 \frac{1}{2}\left(\frac{4}{3}\cdot\frac{\eta}{\rho} + \frac{\eta'}{\rho} + \nu\left(\frac{C_p - C_v}{C_p}\right)\right),$$

where α is the damping coefficient of sound; a, the velocity of sound; η and η', the ordinary and second viscosity coefficients; ρ, the density of the

* One of the papers [(1), p. 316] deals with scattering in gases. The faint tone observed in the photomicrograms can be connected with the rotational wings, as well as with the widening of the Rayleigh line itself [2].

liquid. It is clear from the above that the ratio of the intensity of the central line at maximum $\left(\text{i. e., } I(0)=\frac{I\pi}{\delta}\right)$ to the sum of the maximum intensities of the doublet components equals:

$$\left(\frac{I_c}{I_d}\right)_{\max}=\frac{C_p-C_v}{C_v}\cdot\frac{\delta_d}{\delta_c}=\frac{C_p-C_v}{C_v}\cdot\frac{\frac{4}{3}\frac{\eta}{\rho}+\frac{\eta'}{\rho}+\nu\left(\frac{C_p-C_v}{C_v}\right)}{2\nu}. \qquad (2)$$

However, the ratio of the maximum intensities of the central line and the components of the doublet measured in (1) (p. 336 and 352) can be compared neither with formula (1), nor even with formula (2), for due to the different widths of these lines they are differently modified by the interferometer. Nevertheless, several conclusions based on the experimental data for alcohols [(1), p. 352] can be drawn. In liquids of small viscosity the relaxation of processes of the Kneser type which causes the appearance of the second coefficient of viscosity takes place at frequencies $\sim 10^9$ (4). Hence the damping of sound of frequency

$$\omega=\frac{2\pi a}{\Lambda}\sim 4\cdot 10^{10}$$

which is essential for questions of scattering, is determined mainly by the ordinary viscosity η. Furthermore, in liquids of small viscosity at $\omega\sim 4\cdot 10^{10}$ there is no relaxation of the ordinary viscosity, and the quasi-static value may be taken for η in (2). For the series of alcohols investigated $\nu\sim 0.001$, $\rho\sim 0.8$ and η varies from the value 0.005 for methyl alcohol to the value $\eta=0.029$ for isobutyl alcohol. Accordingly, the ratio computed from (1) varies from 0.205 to 0.16, while the experimentally measured ratio varies from 0.285 to 0.66. It follows from the foregoing that the measured ratio should grow with an increase of η, what it actually does in experiment, whereas the ratio (1) decreases.

Also the results of the temperature measurements [(1), p. 329] can be understood, if the dependence of the relaxation time for the second viscosity on the temperature [case of acetone (4)], the dependence of the ordinary viscosity on the temperature (case of phenol), and the possible change of ν and C_p/C_v with the temperature are taken into account.

Relaxation of the Kneser type should lead to an increase in the velocity of sound. From the new measurements of the velocity of sound in the region of frequencies $\omega\sim 10^{10}-10^{11}$ [(1), p. 371] which are in quantitative disagreement with the experiments of Rao discussed by me (5), one can conclude that the change in velocity does not exceed several per cent. Nor is there any ground for expecting a greater change due to relaxation of the Kneser type and the processes pointed out in (5). Hence the question of the dispersion of sound in liquids of small viscosity remains open.

In viscous liquids (glycerine, castor oil) the ordinary viscosity relaxes at $\omega<10^{10}$, thus, with respect to waves of $\omega\sim 10^{10}-10^{11}$ these liquids act like amorphous solids. Transverse waves can be propagated in these liquids; hence the spectrum of the scattered light may contain yet another doublet situated within the main one. The proximity of the components of this doublet to the central line, as well as the possibly large width of the components makes their observation difficult. It is useful to bear in mind in experimenting that the lines of the second doublet are highly depolarized.

Venkateswaran observed the appearance of faint satellites at a distance equal to twice the distance between the central line and the components of the main doublet [(1), p. 327]. This effect cannot be explained by secondary scattering, since when the scattering angle is $\sim 180°$, as is the case in the experiment, the maximum spectral displacement of the doubly scattered rays

is only approximately 1.4 times greater than normal. The origin of satellites remains uncertain.

The scattering of light takes place as a result of the fluctuation of the dielectric constant* ε. For an isotropic body in equilibrium the dielectric constant is a scalar; but when fluctuations occur, the body becomes anisotropic and its optical properties are characterized by a tensor ε_{ik}. The fluctuations of ε_{ik} can be written in the form; $\Delta\varepsilon_{ik} = \Delta\varepsilon\delta_{ik} + \Delta\varepsilon'_{ik}$, where $\sum_i \Delta\varepsilon'_{ii} = 0$ and, evidently, $\varepsilon_{ik} = \Delta\varepsilon'_{ik}$ when $i \neq k$. The «anisotropy fluctuations» $\Delta\varepsilon'_{ik}$ which call forth the appearance of the depolarized «wings» of the line in the Rayleigh scattering of light in liquids are not directly connected with the fluctuations of the density $\Delta\rho$ and of the temperature ΔT, since the latter do not destroy the anisotropy of the liquid. In order to compute $\Delta\varepsilon'_{ik}$ it is therefore necessary to make special assumptions regarding the connexion between this tensor and the variation in the free energy of the liquid upon its deviation from the equilibrium state [see, for example, (6)]. The fluctuations $\Delta\varepsilon$, on the contrary, depend on $\Delta\rho$ and ΔT:

$$\Delta\varepsilon = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \Delta\rho + \left(\frac{\partial\varepsilon}{\partial T}\right)_\rho \Delta T.$$

This relation should also take into account the possible dependence of $\Delta\varepsilon$ on parameters which describe the liquid in a non-equilibrium state. The corresponding part of $\Delta\varepsilon$ should, evidently, be exceedingly small in comparison with $\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \Delta\rho$ (but not with $\Delta\varepsilon'_{ik}$). The same is apparently true of $\left(\frac{\partial\varepsilon}{\partial T}\right)_\rho \Delta T$, and it may, therefore, be assumed that $\Delta\varepsilon \leqq \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \Delta\rho$. Thus the fluctuations $\Delta\varepsilon$ are determined by isothermic density fluctuations. The attempt to reconsider this well-known fact [(1), p. 340] is entirely unfounded**. Assuming the relation $\Delta\varepsilon = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \Delta\rho$, one can deduce Einstein's (7) formula for the scattering intensity. Scattering on anisotropy fluctuations is usually taken into account by introducing the factor

$$\frac{1+\Delta}{1+\frac{7}{6}\Delta}$$

where Δ is the depolarization of the scattered natural light. In order to arrive at this factor it must be assumed that for scattering, connected with anisotropy fluctuations, depolarization equals 6/7, an assumption which is theoretically unfounded. The formula for the scattering intensity contains the quantity $\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_T$ which is usually expressed in terms of $\varepsilon = n^2$ by means of a relation of the type of the Lorentz—Lorenz formula. Such a procedure, however, is out of place, inasmuch as no theoretical basis can be found for the Lorentz—Lorenz and other formulae, nor are they borne out by experiment. The only trustworthy method, therefore, consists in utilizing the experimental values of $\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T$. The cause of the disagreement between the experimental data [(1), p. 347] and the results of computations based on Einstein's formula with utilization of the measured values of $\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T$ remains unclear.

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* ε is understood to mean the square of the refractive index n for a given wave-length of light.

** It is assumed, for example, that $\overline{\Delta\rho\Delta s} = 0$ (Δs is the entropy fluctuation), whereas $\overline{\Delta\rho\Delta s} = -\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial\rho}{\partial p}\right)_T kT$, where p is the pressure.

The spectrum of the scattered light is determined by the kinetics of the fluctuations $\Delta\varepsilon_{ik}$ or, to be more exact, of the space Fourier component of these fluctuations corresponding to the ware-length Λ. The isothermal fluctuations of density to which the principal part of $\Delta\varepsilon$ is proportional, can be represented as the superposition of adiabatic fluctuations of ρ propagated with the velocity of sound, and isobaric fluctuations of ρ which call forth the appearance of the central line. The kinetics of the fluctuations $\Delta\varepsilon'_{ik}$ and the fluctuations $\Delta\varepsilon$ which are not connected with $\Delta\rho$ cannot be investigated without special assumptions. One thing only is clear: that the main time determining the spectral composition of light scattered on anisotropy fluctuations in liquids of low viscosity, is the Debye time of relaxation

$$\tau = \frac{4\pi r^3 \eta}{3kT}$$

where r is the «molecular radius» ([3],[6],[8]). This time $\tau \sim 10^{-12}$, hence the width of the depolarized «wings» of the Rayleigh line in liquids $\Delta\omega \sim 10^{12}$ ([8],[9])*. The time of relaxation for the anisotropy fluctuations should coincide with the time of relaxation for the Kerr effect. However, as Fabelinsky ([9]) has stressed, this latter time is $\sim 10^{-9}$. Thus, in addition to processes with a time of relaxation $\sim 10^{-12}$ there should also be processes taking place in the liquid with a time of relaxation $\sim 10^{-9}$. This circumstance is borne out by the fact that the central scattering line is depolarized [([1]), pp. 329 and 357], whereas the lines of the doublet are completely polarized. Indeed, if the anisotropy fluctuations died down in a time $\tau \sim 10^{-12}$, the intensity of the light scattered on them should be approximately the same in the region of the central line and in the region of the doublet components, since $\tau \ll \frac{1}{\omega}$, where ω is the spectral width of the doublet. The mechanism of relaxation in a time $\sim 10^{-9}$ is not clear. We observe that, as follows from the expression for the Debye time of relaxation, a change in the radius r of 10 times its value (dust, molecular complexes and groups) is already sufficient to bring about a change in τ of 1000 times its value. With respect to the question of the two times of relaxation, wide possibilities are open: determination of the form of the decay function for the Kerr effect for the purpose of establishing the ratio of processes with $\tau \sim 10^{-9}$ and $\tau \ll 10^{-9}$, establishment of the correlation between the depolarization of the central line and the part played by slow processes in the decay of the Kerr effect, etc.

I am grateful to Prof. L. D. Landau for discussion of the problems touched in this paper.

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Received
5. VIII. 1943.

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* In addition to the spectrum of anisotropy fluctuations, the combination (Raman) spectrum of the liquid is also represented in the «wings»([8]).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PHYSICS

POINT SOURCE OF LIGHT BETWEEN PARALLEL PLANES

By V. V. SOBOLEV

(Communicated by S. I. Wawilow, Member of the Academy, 22.X.1943)

If a luminous source is placed near to reflecting surfaces, the illuminations cannot be properly ascertained without taking into account the repeated reflections from these surfaces. Generally speaking, the problem is reduced to the solutions of an integral equation.

Below is discussed a case when the solution of the integral equation is obtained in the explicit form.

Let us consider a point source of light placed between two parallel ideally reflecting planes (e. g., in first approximation a flare bomb between clouded sky and Earth surface). Suppose that the light intensity of the source is independent of direction, and the space between the planes is perfectly transparent.

Let H be the distance between the planes; h_1 and h_2, the distances of the source from the respective planes; ρ_1 and ρ_2, the coefficients of reflection of the planes; I, the light intensity of the luminous source; r, distance of some point from the perpendicular drawn to the plane through the source; $E_1(r)$ and $E_2(r)$, illuminations of the planes, in the finding of which consists the problem.

On either plane we take orthogonal coordinates with centres at the intersection point of the planes with the perpendicular just mentioned. It may easily be derived that the illumination of the first plane is

$$E_1(r) = \frac{\rho_2}{\pi} H^2 \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} \frac{E_{21}(r')\,dy'}{[H^2 + (x-x')^2 + (y-y')^2]^2} + \frac{I h_1}{(h_1^2 + r^2)^{3/2}} \qquad (1)$$

in the case of the second plane we obtain an analogous expression for $E_2(r)$]. in the subsequent we assume that $I = 1$ and $H = 1$. This will mean that the illuminations are expressed in terms of the ratio I/H^2 as a unit.

In order to solve the obtained system of integral equations we introduce instead of $E_1(r)$ a new quantity $G_1(x)$ equal to

$$G_1(x) = \int_{-\infty}^{-\infty} E_1(r)\,dy. \qquad (2)$$

As the equation (2) is an integral equation of Abel, we have

$$E_1(r) = -\frac{1}{\pi} \int_r^{\infty} \frac{G_1'(x)\,dx}{\sqrt{x^2 - r^2}} \qquad (3)$$

On physical considerations it is apparent that the quantity $G_1(x)$ does not depend on the distribution of brightness along the axis OY. This implies the existence for this quantity of an integral equation with a kernel depending solely upon the difference $x' - x$. Indeed, we find after integrating (1) over y that

$$G_1(x) = \frac{\rho_2}{2} \int_{-\infty}^{+\infty} \frac{G_2(x')\,dx'}{[1+(x'-x)^2]^{3/2}} + 2\frac{h_1}{h_1^2+x^2}. \tag{4}$$

We introduce the notations

$$\Phi(t) = \int_0^{\infty} \frac{\cos xt}{(1+x^2)^{3/2}}\,dx; \tag{5}$$

$$\varphi_1(t) = \int_{-\infty}^{+\infty} G_1(x)\,e^{-ixt}\,dx. \tag{6}$$

And then we get from (4)

$$\varphi_1(t) = \rho_2\varphi_2(t)\,\Phi(t) + 2\pi e^{-h_1 t}. \tag{7}$$

Writing the corresponding expression for $\varphi_2(t)$ and solving the obtained system with respect to $\varphi_1(t)$ and $\varphi_2(t)$, we find

$$\varphi_1(t) = 2\pi \frac{e^{-h_1 t} + \rho_2 e^{-h_2 t}\Phi(t)}{1-\rho_1\rho_2\Phi^2(t)}. \tag{8}$$

The inversion of the Fourier equation (6) and the use of (8) and (3) gives

$$E_1(r) = \int_0^{\infty} \frac{e^{-h_1 t} + \rho_2 e^{-h_2 t}\Phi(t)}{1-\rho_1\rho_2\Phi^2(t)}\,I_0(rt)\,t\,dt \tag{9}$$

where $I_0(x)$ is a Bessel function of order zero.

Formula (9) is the final solution of the problem.

It may be noted that the method described in this paper is also applicable in the following cases:

1) The radiation of the source is symmetrical with respect to the line drawn through it perpendicular to the planes.

2) The space between the planes is filled with absorbing (but not scattering) medium.

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Received
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

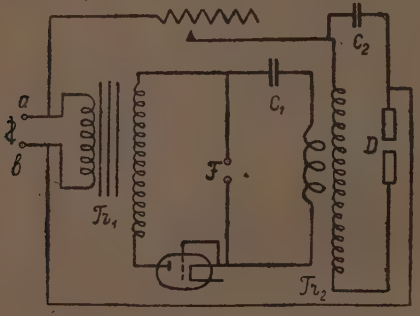
TECHNICAL PHYSICS

ARC RECTIFIER OF ALTERNATING CURRENT

By S. A. BOROVICK

(Communicated by S. I. Wawilow, Member of the Academy, 15.VII.1943)

In the experiments which have been carried out with an a. c. activated arc, it proved to be possible to use a similar scheme for rectification of the alternating current. For this reason an electron tube (see figure) is introduced into a high voltage circuit. One phase of the alternating current is delayed by this tube. The arc between iron electrodes begins to burn in time with these interruptions, whereby the rectification of the current is brought about. In the figure *a*, *b* are clamps of alternating current; Tr_1, transformer of low frequency; ГК-20, a cathode lamp; F, spark gap; C_1, C_2, condensers; Tr_2, transformer of high frequency; D, arc between iron electrodes.



In our experiments we have used an electronic tube ГК-20. Its grid was joined to an incandescent filament which was heated by separate transformers, not shown in the figure. The supplementary expenditure of energy is very small; the rectification, complete; the cross-section of iron electrodes can be so selected as to bring the strength of the rectified current up to several tens of amperes.

The advantage of this system as compared to the mercury rectifier is that the burning is started simply by switching on the tube without swinging; yet, it is less economical, since the voltage drop on the electrode in an arc is greater in the air than in rarefied mercury vapour; easy restoration of the device is another great advantage of this system of rectification. In order to smooth out the pulsations of the alternating current, one can set up two arcs, using both phases as well as throttles. This device is more complicated, but neither more costly nor larger in size than a similar device with a mercury rectifier.

Instead of an electron tube one can use an interrupter mounted on the axis of a synchronous motor.

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Received
15. V. 1943.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

CHEMISTRY

CLEAVAGE OF THE CARBON CHAIN OF α-METHYL-*d*-GLUCOPYRANOSIDE IN AMMONIACAL CUPRIC SOLUTION

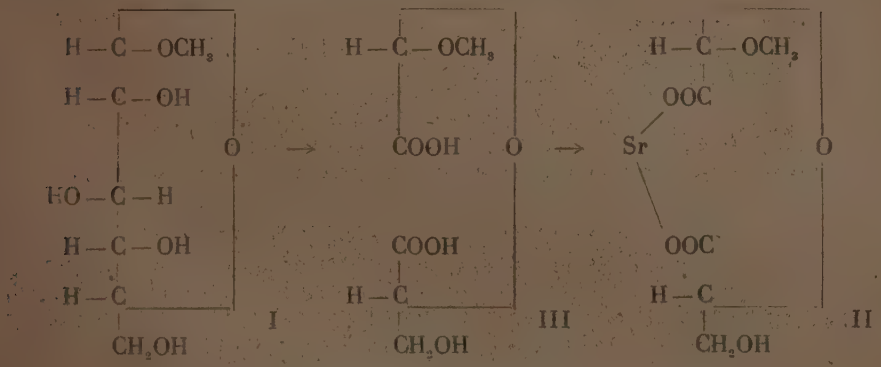
By V. I. IVANOV

(Communicated by A. E. Arbusov, Member of the Academy, 5.V.1943)

It is recognized [2–4] that when glucopyranosides are oxidized by periodic acid or barium hypobromite in aqueous solutions, a rupture of carbon chain takes place to form dibasic acids.

We have adopted a method of oxidation of α-methyl-*d*-glucopyranoside (I) by atmospheric oxygen in ammoniacal cupric hydroxide medium *.

The investigation resulted in establishing the fact that in one of the directions the reaction proceeds according to the scheme:



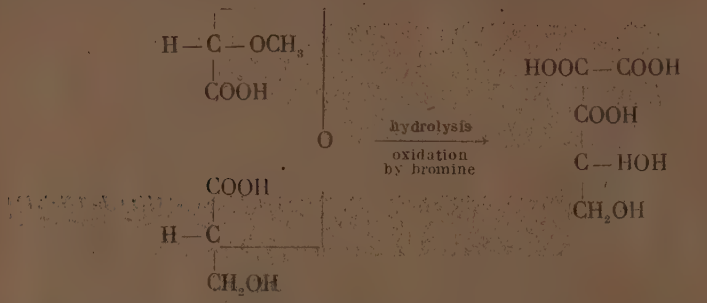
D'-Methoxy-*D*-hydroxymethyl-diglycolic acid (III)

The acid (III) has been isolated as its strontium salt (II). The analysis of the strontium salt has shown:

	Calcd. for $C_6H_8O_7Sr$	Found I	Found II
C	25.74%	25.40%	25.17%
H	2.88%	2.87%	2.89%
Sr	31.33%	29.25%	29.44%
OCH_3	11.10%	11.88%	10.96%

* The experimental part has been accomplished with the assistance of K. M. Sokova.

From the strontium salt diglycolic acid of the formula (III) has been isolated which was subsequently hydrolysed and oxidized by bromine. As the result, oxalic and glyceric acids have been obtained:



The oxalic acid has been isolated as its calcium salt and converted into the free acid with m. p. 100 to 101°.

	Calcd. for $C_2O_4Ca \cdot 3H_2O$	Found I	Found II
C	13.18%	12.83%	13.63%
H	3.29%	2.79%	3.27%
Ca	21.97%	22.46%	22.15%

The glyceric acid has also been isolated as its calcium salt with m. p. 141 to 142°.

	Calcd. for $C_6H_{10}O_8Ca \cdot 2H_2O$	Found I	Found II
H_2O	12.59%	12.63%	—
Ca	14.00%	13.95%	13.76%

We have selected methyl-glucopyranoside since we considered it as an elementary analogue of the structural unit of cellulose, as well as a representative of a group of substances which play an important rôle in nature.

On the basis of the presented data we advance a conjecture that in ammoniacal cupric hydroxide solution the structural units of macromolecules of cellulose may be chemically converted under the influence of atmospheric oxygen.

This conjecture has incited us to reconsider critically the opinion, current in scientific literature, that there is no chemical conversion of the macromolecules of cellulose when the latter is dissolved in the Schweitzer reagent.

We now take the opportunity to emphasize the fact that the oxidating processes accompany the majority of technological operations connected with manufacturing and further treatment of cellulose (production of cellulose from wood, bleaching, preparation of xanthogenic esters of cellulose, treatment of cotton stuff products, etc.); these processes lead to certain alterations of physico-chemical and physico-mechanical properties of cellulose fibre as well as of the final products. A considerable number of experimental work devoted to the study of the constitution of cellulose and particularly to determination of its molecular weight are based on the investigation of its solutions in Schweitzer's reagent.

Nevertheless, very little is known about the oxidating processes which take place in ammoniacal cupric hydroxide solutions (1).

Therefore, the study of chemical transformations of macromolecules of cellulose under the influence of oxidants is of considerable practical and of no less

theoretical interest. A study of oxidation cracking of cellulose must, to our opinion, give rise to guiding theoretical ideas, and above that open extensive possibilities for utilizing the cracking products of cellulose for heavy organic synthesis.

Further experimental work is in progress involving studies on the transformations of macromolecules of cellulose in ammoniacal cupric hydroxide solutions and the oxidation of glucosides by various oxidants.

Conclusions

1. It has been shown that, when α-methyl-*d*-glucopyranoside is oxidized by atmospheric oxygen, cleavage of carbon chain with the formation of *D'*-methoxy-*D*-hydroxymethyl-diglycolic acid is one of the directions of the reaction.

2. An opinion has been advanced in contrast with one current in scientific literature that chemical transformations of elementary structure units of the macromolecule of cellulose may take place when the latter is being dissolved in ammoniacal cupric hydroxide solution in the presence of the air.

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Received
5. V. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

CHEMISTRY

ON THE INTERACTION OF THIOSULPHATE WITH CERTAIN SALTS OF PLATINUM

By D. I. RIABCHIKOV

(Communicated by A. E. Arbusov, Member of the Academy, 19. IV. 1943)

1. It was found to be impossible to obtain thiosulphate compounds with tetravalent platinum, owing to reduction of the platinum ($Pt^{++++} \rightarrow Pt^{++}$) by the thiosulphate ion.

The reduction process proceeds quite readily even under ordinary conditions. For example, the addition of a sodium thiosulphate solution to the yellowish-orange solution of sodium chloroplatinate ($Na_2[PtCl_6]$) immediately causes a change in the initial colour: the solution takes on a pinkish hue, characteristic of chloroplatinates ($Na_2[PtCl_4]$).

The presence of this latter form in the solution is easily proved by the formation of the green Magnus salt $[PtCl_4]\,[Pt4NH_3]$ under the action of salt of the Reiset I base. The $[PtCl_4]^{=}$-ion could form in the solution only as a result of the reduction of the initial $[PtCl_6]^{=}$-ion upon interaction with thiosulphate according to the reaction:

$$Na_2[PtCl_6] + 2Na_2S_2O_3 \rightleftharpoons Na_2[PtCl_4] + Na_2S_4O_6 + 2NaCl.$$

The sodium thiosulphate is thereby oxidized to tetrathiosulphate.

The process of the reduction of tetravalent platinum is not affected by the nature of the coordination groups.

Besides sodium platinate, we employed the sparingly soluble salt of Gros $[Pt4NH_3Cl_2]\,Cl_2$. Its precipitate in a solution of sodium thiosulphate dissolved very quickly.

With this $[Pt4NH_3]^{++}$-ions form in the solution, which are obtained by the reduction of the $[Pt4NH_3Cl_2]^{++}$-ions by thiosulphate according to the reaction:

$$[Pt4NH_3Cl_2]\,Cl_2 + 2Na_2S_2O_3 \rightarrow [Pt4NH_3]\,Cl_2 + Na_2S_4O_6 + 2NaCl.$$

The presence in the solution of $[Pt4NH_3]^{++}$-ions is easily detected upon the addition of potassium chloroplatinate, since in this case also the green Magnus salt separates out.

If now the solutions that have formed upon the action of thiosulphate on sodium chloroplatinate and the Gros salt are united, interaction will take place between their reduction products, according to the reaction:

$$Na_2[PtCl_4] + [Pt4NH_3]\,Cl_2 \rightarrow [PtCl_4]\,[Pt4NH_3] + 2NaCl.$$

And the same green Magnus salt is carried down again.

We attempted to use the reaction of the reduction of tetravalent platinum by thiosulphate for its quantitative determination during potentiometric titration.

Such an attempt of a volumetric determination of platinum by titration with thiosulphate in the presence of potassium iodide was made by Peterson as far back as in 1899(1).

We performed the titration without starch until the appearance of a lemon-yellow colour, and believed the reaction to be directed as follows:

$$a)\ PtCl_4 + 4KI \rightarrow PtI_2 + I_2 + 4KCl$$

$$b)\ I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6.$$

The investigations of Grünberg and Ptitzin(2), which were carried out under similar conditions; did not confirm the presence of free iodine in the solution. In the light of recent data it may be assumed that in reality the interaction process in the experiments of the indicated authors proceeded thus:

$$a)\ Na_2[PtCl_6] + 6KI \rightarrow Na_2[PtI_6] + 6KCl$$

$$b)\ Na_2[PtI_6] + 6Na_2S_2O_3 \rightarrow Na_6[Pt(S_2O_3)_4] + Na_2S_4O_6 + 6NaI.$$

As a matter of fact; the rôle of KI differs from that assumed by Peterson. The iodoplatinate that forms as a result of the presence of KI in the solution still more energetically interacts with the thiosulphate ions. The reaction goes on after the reduction of platinum to a bivalent state has taken place and eventually the internal sphere of the complex is entirely substituted with $S_2O_3^=$groups. The lemon-yellow colour of the solution to which the titration was carried out by those authors appears as a result of the formation in the solution of thiosulphatoplatinite.

The insufficient accuracy of the results of a determination according to this method is possibly due to the fact that at small concentrations of the interacting products interaction may take place with a smaller amount of thiosulphate as well.

The result is that compounds are obtained with a smaller number of $S_2O_3^=$groups in the internal sphere: $Na_4[Pt(S_2O_3)_3]$; $Na_2[Pt(S_2O_3)_2]$; as I have established (3).

Titration of tetravalent platinum salt with a thiosulphate solution, which I largely undertook for the same reason without the addition of Kl, did not lead to positive results.

2. The action of thiosulphate on certain coordination polymers indicates an essential difference in the firmness of the bond of the different groups of the internal sphere.

Thus, if the green Magnus salt $[PtCl_4][Pt4NH_3]$ is added to a sodium thiosulphate solution heated up to boiling, this salt is observed to dissolve quite rapidly. The solution becomes yellow, and a bright yellow crystalline precipitate separates out from it.

As a result of the reaction, replacement of the chlorine atoms by thiosulphate residues takes place in the anion of this salt; in the cation, on the other hand, this does not occur. Formation of a polymer of a new composition takes place in the solution, which, owing to its very slight solubility, precipitates out, and there accumulates an excess of the soluble form of the thiosulphate compound. The reaction takes place according to the equation:

$$3[PtCl_4][Pt4NH_3] + 12Na_2S_2O_3 \rightarrow$$
$$\rightarrow [Pt(S_2O_3)_4][Pt4NH_3]_3 + 12NaCl + 2Na_6[Pt(S_2O_3)_4].$$

In the presence of a large excess of thiosulphate and upon prolonged heating the precipitate of the composition $[Pt(S_2O_3)_4][Pt4NH_3]_3$ that has separated out may also dissolve. In such a case replacement of the ammonia molecules by thiosulphate residues occurs in the cation of the salt. The ammonia is evolved in the free state, while in the solution there is obtained only the soluble form—soduim thiosulphatoplatinite $Na_6[Pt(S_2O_3)_4]$. A quite identical picture is observed if we start from the oxalate form of the polymer of the composition $[Pt(C_2O_4)_2]$.

$[Pt4NH_3]$. In the case of this compound substitution in the anion takes place even at slight heating.

Somewhat different is the process of interaction of excessive thiosulphate with the polymers, the cation of which is formed with molecules, less firmly linked to the central platinum atom than ammonia. Thus, if during heating one acts even with a small excess of sodium thiosulphate on a salt of the composition $[PtCl_4]$ $[Pt4C_5H_5N]$, then no precipitate whatsoever forms and the solution smells strongly of pyridine, which testifies that the internal sphere of the complex is replaced by this salt at once in both the anion and cation. The process proceeds according to the equation:

$$[PtCl_4]\ [Pt4C_5H_5N] + 8Na_2S_2O_3 \rightarrow 2Na_6\ [Pt(S_2O_3)_4] + 4NaCl + 4C_5H_5N.$$

It is interesting to note that a salt of the composition $[PtCl_4]$ $[Pt4SCN_2H_4]$ in this respect shows exactly the same behaviour with its pyridine analogue.

At a temperature of about 75° C the precipitate dissolves, and a yellow solution is formed that contains the salt $Na_6[Pt(S_2O_3)_4]$. Substitution takes place in the same way in both parts of the molecule. However, with deficiency of thiosulphate substitution takes place only in the anion, and, what is more, the S_2O_3-groups occupy two coordination positions each.

The reaction takes place according to the equation:

$$[PtCl_4]\ [Pt4SCN_2H_4] + 2Na_2S_2O_3 \rightarrow [Pt(S_2O_3)_2]\ [Pt4SCN_2H_4] + 4NaCl.$$

The flake-like precipitate of the composition $[Pt(S_2O_3)_2]$ $[Pt4SCN_2H_4]$ that separates out, crystallizes after standing in the mother liquor for a protracted period of time.

Conclusions

1. It is impossible to obtain thiosulphate complex compounds of tetravalent platinum, owing to its easy reduction by thiosulphate to the bivalent state.

2. The reaction of the reduction of tetravalent platinum by thiosulphate cannot be used for a quantitative determination, since the reaction with the thiosulphate proceeds further up to formation of the complex, and in this respect the process may stop at various degrees of saturation of the internal sphere of the platinum with thiosulphate residues.

3. The thiosulphate has been found to act differently on coordination polymers according to the firmness of the link of the substitutent in the internal sphere.

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Received
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PHYSICAL CHEMISTRY

THEORY OF OXIDATION OF IRON-CHROMIUM-ALUMINIUM SOLID SOLUTIONS

By I. I. KORNILOV

(Communicated by V. G. Chlopin, Member of the Academy, 28/VIII.1943)

1. In one of his previous works the author (1) put forward the principal statements of the oxidation theory of iron-chromium-aluminium alloys corresponding to a solid solution.

The character of this oxidation process can be represented schematically as follows:

$$2(Al, Cr, Fe) + 4\tfrac{1}{2}O_2 \rightarrow Al_2O_3 + Cr_2O_3 + Fe_2O_3 \quad (1)$$

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \quad (2)$$

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \quad (3)$$

The first of these reactions (1) refers to the interaction of iron-chromium-aluminium alloys with the oxygen of the air as observed at moderate temperatures and during the early stages of oxidation at high temperatures.

The second and the third present an ordinary alumo-thermal reduction of chromium and iron oxides by aluminium. They take place in the surface layer of the alloy at the sites of contact of these oxides with the aluminium atoms.

As a result of the partial reaction (1) (the oxidation of aluminium by the oxygen of the air) and the reactions (2) and (3) (oxidation of aluminium by the oxygen of chromium and iron oxides) the concentration of aluminium in the surface layer of the ternary alloy undergoes a decrease by oxidation, and accordingly more aluminium oxide is formed on the surface. This process disturbs the homogeneity of the alloy as regards its chemical composition, and the content of aluminium in our ternary solid solution shows a change. As the surface layer of the alloy grows gradually lower in aluminium, the system becomes less and less stable thermodynamically. It has a tendency under these conditions to alter the aluminium concentration in the alloy spontaneously. There begins a diffusion of aluminium from the inner layers with higher concentration to the poorer outer layer. These conceptions have found confirmation in the experiments with ternary iron alloy containing 27 per cent of chromium, 5.8 per cent of aluminium. A specimen of circular cross-section, 16 mm in diameter, was allowed to suffer oxidation at 1200° C for 100 and 500 hours. The results are brought out by the curves of Fig. 1. They show that the relative decrease in aluminium across the section is in the direction of the diffusion of aluminium from the rich central to the poor outer layer. After 500 hours the picture of the decrease of aluminium content across the alloy specimen was the same as after 100 hours.

When the curves of diffusion of aluminium from our ternary solid solution in the process of oxidation are compared with curves bringing out an ordinary

Nos.	Duration of experiment in hours	Chemical composition and electric resistivity ρ (ohm.mm²/m) of ternary solid solution in relation to time oxidation at 1200°C													
		18% Cr; 3.00% Al			18% Cr; 5.45% Al			18% Cr; 9.8% Al			17% Cr; 12% Al			17% Cr; 15% Al		
		Cr	Al	ρ	Cr	Al	ρ	Cr	Al	ρ	Cr	Al	ρ	Cr	Al	ρ
1	0	18.90	3.0	1.15	18.60	5.40	1.50	17.06	9.80	1.90	16.05	11.08	2.01	17.0	15.00	—
2	96	18.95	2.97	1.01	18.60	5.38	1.25	16.98	9.78	—	16.06	16.48	—	16.48	—	—
3	144	18.89	2.16	0.96	19.53	5.25	1.23	16.98	8.20	1.77	16.62	11.06	2.00	—	14.79	—
4	240	18.97	1.93	0.93	18.68	4.58	1.19	16.98	7.89	1.67	16.81	10.92	1.98	15.48	13.76	—
5	500	18.95	1.89	0.84	18.62	4.55	1.12	16.98	8.17	1.58	17.98	11.03	1.98	16.00	14.92	—
6	700	18.60	1.78	0.84	18.42	3.86	1.13	16.98	8.13	1.60	16.80	10.57	—	16.00	14.60	—
7	1000	—	1.32	—	18.80	3.21	0.97	17.20	7.60	—	16.44	9.73	1.91	16.34	14.39	—
Decrease of Al in % to initial content		—	56	—	—	40	—	—	22.5	—	—	12	—	—	5	—

diffusion of one metal into another (such as results in the formation of solid solutions of the two metals), it becomes apparent that the diffusion of aluminium in our case obeys the Fick law (2) for ordinary diffusion. The only difference is that in the case of ordinary diffusion the alien atoms move from the surface to inner layers, whereas the movement of aluminium within the solid solution under consideration is in the opposite direction.

In connexion with studying the oxidation of ternary alloys and the aluminium diffusion phenomena at high temperatures it appeared of interest to establish, how the rate at which aluminium is oxidized is influenced by its concentration in the ternary solid solution. The relative velocity of oxidation was determined from the lo s of weight, the change of electric resistivity and the data of chemical analysis on the total content of aluminium. Two sets of ternary alloys were

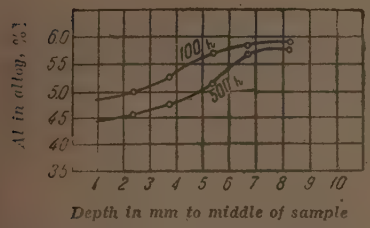

Fig. 1. Diffusion of aluminium in the process of oxidation of ternary alloy with 67 per cent Fe, 27.0 per cent Cr, 5.8 per cent Al in the air at 1200°C

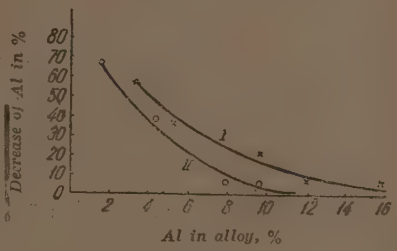

Fig. 2. Rate of aluminium loss by oxidation in Fe-Cr-Al solid solutions at 1200°C for 1000 hours

taken for the experiment. I with 17—18 per cent of chromium and 3, 5, 9, 11 and 15 per cent of aluminium; II with 25—27 per cent of chromium, 1.5, 4.5, 7.5 and 9.5 per cent of aluminium. Subjected to the oxidation (1200° C for 1000 hours) were cylindrical specimens, 3 mm in diameter and 50 mm long. The method was similar to that used by us in testing iron-chrome-aluminium alloys for thermostability (3). During the experiment, two samples were taken periodically from each set for parallel determinations of properties and chemical composition.

The tabulated data on the content of chromium and aluminium and on the change of electric resistivity in the process of oxidation refer to the first set of alloys.

Instead of separate determinations of aluminium in the different layers of the alloy, as made ordinarily in studying diffusion, I give here the total content of aluminium in the course of the oxidation process, compared to the initial content of this element in the alloy. As might well be anticipated, the continuous decrease of aluminium content in the alloy during the oxidation is paralleled by a gradual decrease in electric resistivity. Such a relationship between the composition and the just mentioned property of the investigated system is in full accord with the «composition—resistivity» diagram obtained for this ternary solid solution (1).

The simultaneous decline of electric resistivity and of aluminium content as oxidation goes on in the two sets of alloys is evidence that the process of oxidation in them has a variable course according to the content of aluminium.

The influence of the concentration of aluminium upon the decrease of the content of aluminium in the samples exposed to oxidation at 1200°C for 1000 hours is illustrated by two curves in Fig. 2. Curve *I* shows that among the alloys containing 15—17 per cent of chromium the maximum decrease of aluminium content (56 per cent) is with the alloy that contained initially 3 per cent of aluminium. The alloy whose initial content of alluminium had been 5 per cent lost only 40 per cent of it by oxidation, and that with 9 per cent of Al lost 22.5 per cent. When the initial concentration of aluminium is increased to 11 and 15 per cent,

the loss by oxidation drops to 12 and 5 per cent respectively. A similar character has the curve *II* which refers to alloys with 25—27 per cent of Cr and a variable content of Al (up to 10 per cent).

To sum up, the higher the initial concentration of aluminium in the solid solution, the slower the relative rate of its loss by oxidation and hence the stronger the thermostability of the alloy. The latter conclusion is in complete agreement with experimental data on the thermostability of ternary solid solutions of these alloys [3].

Conclusions

1. A theoretical conception is given of the character of the oxidation reaction in the ternary solid solutions of iron-chromium-aluminium.

2. The oxidation process at high temperatures is conceived to be made up of two consecutive processes: the primary process of oxidation of all the three metals—Al, Cr and Fe—on the surface, and the secondary process consisting in the diffusion of aluminium caused by its selective oxidation on the surface of the alloy.

3. It has been proved by studying the diffusion of aluminium in the process of oxidation that the concentration of this element in the alloy gradually declines as we follow it from the surface to the central layers.

4. By the method of physico-chemical analysis the existence of a relationship has been established between the loss of aluminium by oxidation and the initial concentration of this element in the ternary solid solution.

5. With the increase of aluminium content in this solid solution the rate of its oxidation is slowed down.

6. The oxidation processes show a lower rate in concentrated solid solutions of Fe-Cr-Al than in dilute solutions.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

GEOCHEMISTRY

CONTRIBUTION TO THE METHODICS OF RADIOACTIVITY MEASUREMENTS

I. A NEW TYPE OF COMPENSATION APPARATUS FOR MEASURING IONIZATION CURRENTS

By E. S. STCHEPOTJEVA

(Communicated by V. G. Chlopin, Member of the Academy, 18. V. 1943)

Within recent years descriptions of new methods for radioactivity measurements could often be met with in literature: some of them were more accurate(1) and others more rapid(2) than the procedures actually applied. Nevertheless;

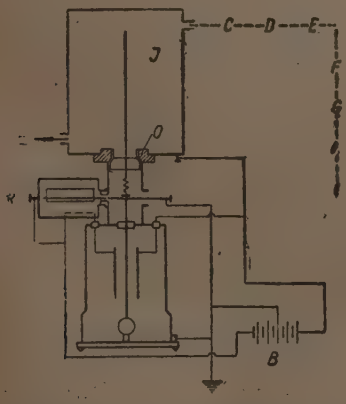

Fig. 1. *K*, compensation chamber; *I*, ionization chamber; *O*, safety ring; *B*, battery of normal cells or accumulators; *C*, metallic tube with cotton, connected to earth or compensation chamber; *D*, tube with calcium chloride and natron-calx; *E*, a three-way glass-tube with two glass-cocks securing passage of air through ionization chamber or outside; *F*, vessel containing solution, placed into special outfit, shaken by a motor; *G*, rheometer; *H*, flask with a tube below and two glass-cocks at the top; *L*, air-blower

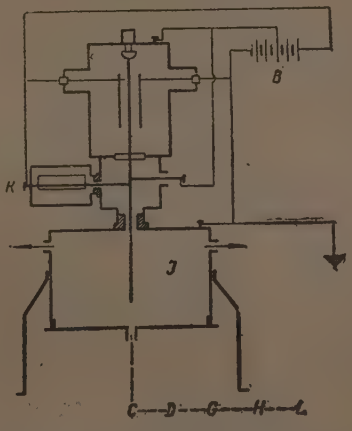

Fig. 2. *K*, compensation chamber; *I*, ionization chamber; *B*, battery of normal cells or accumulators; *C*, metallic tube with cotton, connected to earth or compensation chamber; *D*, tube with calcium chloride; *G*, rheometer; *H*, flask with a tube below and two glass-cocks at the top; *L*, air-blower

when dealing with a number of problems related to the radioactivity; one intensely felt the lack of such methods that would be rapid and sufficiently precise at once. Such methods were particularly missed in geochemical studies; the procedure applied here must be rapid; to ensure a number of measurements sufficient

to arrive at definite conclusions, and sufficiently sensitive, since one often has to measure natural objects of low radioactivity. The method must; besides, be accurate enough.

The new type of compensation apparatus with a small compensation chamber suggested by the author, has been found to answer all the requirements specified above. The idea of the device is made clear by the Figs. 1 and 2.

Fig. 1 shows the scheme of the instrument used for Rn, Tn and An measurements*. As a compensation chamber a small (about 100 cm^3) chamber K is used, which is fixed by means of an ebonite ring to the connexion tube from the electrometer to the ionization chamber. Chamber K has a longitudinal opening along the generatrix of the cylinder, covered with metallic thin foil. Compensation of the background is attained with the aid of β-rays from a small source (uranium oxide, nitrate of uranil, RaE). For less accurate measurements the source may be adjusted in order to obtain desirable compensation simply by hand, after it has previously been fixed in a stand. For measurements of greater precision the source should be placed into a special appliance, fixed to the uncharged part of the apparatus (the electrometer of ionization chamber). It has to be shifted along the opening of the compensation chamber by means of a micrometer-screw.

Fig. 2 illustrates the application of the compensation method for α-ray measurements**. A non-compensation apparatus for α-ray measurements with the aid of one-string electrometer was developed by V. I. Baranov([1]) in collaboration with the author of this article as far back as in 1928.

Compensation apparatus with small compensation chambers, as compared with those generally used having two equal ionization chambers, possess the following advantages: 1) extreme simplicity of construction; 2) simplicity of handling; 3) possibility to work under field conditions; 4) low electrostatic capacity of the instrument, which contributes to its sensitivity; 5) absence of insulator on the compensation chamber ***.

The apparatus ensures simultaneously: 1) a satisfactory sensitivity, as well as 2) sufficient precision and 3) velocity of measurements. Sensitivity is improved by the use of a single-string electrometer with small electrostatic capacity. The precision characterized by the relation of the ionization currents to the magnitude of the background; is determined by the small values of the latter, highly reduced on account of applying the compensation principle. The rapidity of measurements is guaranteed, aside from the use of a sensitive one-string electrometer, by 1) the handiness of the instrument, 2) the possibility (in many cases), instead of measuring, merely of checking up the order of the value of the background, and 3) the application (in the case of Rn measurements) of numerous removable ionization chambers; true enough, one has to content oneself by partial compensation of the background, established according to one of the ionization chambers showing the mean background, but for many operations this is quite sufficient.

The drawbacks of this kind of instruments consist; theoretically; in the two ionization chambers being different in size; hence the impossibility of an automatic compensation for the fluctuations of the background. But in reality the automatic compensation often fails even in case both chambers are equal in size (with local variations in radiation intensities which are the most frequently dealt with). Besides, the radiologist has usually got to work with ionization chambers and in rooms that are rather strongly contaminated with radioactive substances.

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* A part of the set-up serving for a continuous air flow is necessary for measurements of thoron and actinon only. For radon measurements it is convenient to have a chamber that may easily be removed from the electrometer (connexion by means of a small spring). It is expedient also to have several (up to 20) similar removable chambers; amber insulators must be supplied with safety rings ([3]).

** The idea to apply the method of compensation to α-ray measurements belongs to V. I. Baranov upon whose suggestion the author designed the instrument described here as early as in 1938.

*** Hereby is reduced the error due to the leak of the charge through the insulators; the detection of deficient insulator in case insulation proves insufficient is also facilitated.

The main practical object attempted when applying the compensation method comes rather to a sharp reduction of the background proper, than to getting rid of its fluctuations.

All the compensation apparatus described have been thoroughly checked on practical work, partly by the Expedition of this institute, sent to the Caucasian Mineral Waters in 1940 (chief Prof. Starik), partly at the Moscow laboratory, where the material was subjected to treatment. It has been found that measurements made with the help of removable chambers give in the case of radon a precision of 1×10^{-12}—3×10^{-12} Curie (which is a value corresponding to the magnitude of the background of the instrument*). In the case of thoron the precision is 1×10^{-5} g of Th; in the case of α-rays; 3×10^{-5} U_3O_8**. The rapidity of the measurements may be appraised from the fact that within one month it proved possible for us to carry out about 600 measurements for α-rays. During a year we made more than 2000 measurements of radon and thoron, the objects being all of medium and low activity.

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* Working with one chamber it is possible, under favourable conditions, to measure quantities of the order 2×10^{-13} Curie.

** α-ray measurements were carried out in a room with strongly contaminated air, no pure air being blown through the ionization chamber; under favourable conditions the precision may be greatly increased.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

SOIL SCIENCE

ON THE USE OF DATA ON THE AGGREGATE CONDITION OF GROUNDS

By N. J. DENISSOV

(Communicated by V. G. Chlopin, Member of the Academy, 28.VIII.1943)

It is known that some types of loess-like loams are characterized by a considerable disturbance of their coherence when moistened; this is the chief cause of the well-known deformations of these grounds, viz. of subsidences. It may be supposed that the tendency of the subsiding loess-like loams to become disaggregated may be revealed by a system of mechanical analysis. The aggregates of particles in these grounds must be distinguished by a low water-resistance and fall apart after even a short water treatment.

Therefore, an increase of the time of action of some dispersing factor and its intensity, e. g. the substitution of a short agitation with water by prolonged boiling, cannot produce any sharp increase in the amount of clayey particles and, accordingly, a decrease of the quantity of larger particles.

On the basis of the working hypothesis formulated, determinations of the mechanical composition of a number of grounds were carried out, both of those tending to form subsidences and of those definitely non-subsiding. These analyses were preceded by a different preparatory procedure which consisted in a 3-minute agitation with water at a 12-hour boiling. The results of these determinations are characterized by the water-resistance coefficient of aggregates, calculated, similarly to that proposed by I. N. Antipov-Karataev (1), according to the data on the content of the fraction >0.01 mm, obtained both as a result of a 3-minute agitation q_1 and of 12-hour boiling q_2, according to the formula

$$A = \frac{q_1 - q_2}{q_2}.$$

The data obtained, the average of the results of numerous determinations, are tabulated below. They clearly demonstrate the very low water-resistance of the particle aggregates in the subsiding loess-like loams as compared to the loams of a different type, and to clays.

To achieve an almost complete decomposition of the particle aggregates of subsiding loess-like loams it was sufficient to agitate the sample of ground with water for three minutes, while in the development of the aggregates of other grounds such a minimum effect was very slightly pronounced.

Therefore, the average value of the water-resistance coefficient of aggregates for subsiding grounds is much less than for non-subsiding loess-like loams, and so much the more of clays. This inference enables the «water-resistance coefficient of aggregates» to be used for a relative evaluation of the tendency of loess-like grounds to subside.

The conclusions as to the low water-resistance of aggregates of subsiding loess-like loams, which were made simultaneously with the present author (5) by S. V. Astapov (2), disprove the statement of I. P. Gerassimov (3) and I. P. Gerassimov and K. K. Markov (4) as to the extreme stability of aggregates in loesses, which statement is one of the chief arguments in favour of the soil hypothesis of loess formation, developed by these authors.

Results of Determination of the Amount of Skeletal Particles after a Different Preparation of Grounds for Analysis, and Data on the Water-Resistance Coefficient of Aggregates

Type of ground	Number of skeletal particles 0.25—0.01 mm %		Coefficient of water-resistance of aggregates $A = \frac{q_1 - q_2}{q_2}$	
	after a 3-min. agitation q_1	after a 12-hour boiling q_2	for individual specimens	average value for the type of ground
Loess-like loams of the Terek-Kuma steppes (subsiding)	93.7	83.9	0.12	0.14
Do	79.3	64.4	0.21	
Do	79.9	70.8	0.13	
Do	90.0	84.8	0.06	
Loess-like loam, Malo-Kabarda (subsiding)	52.2	44.6	0.17	
Loess-like loam, town of Novocherkassk (non-subsiding)	81.2	46.9	0.74	0.66
Do	80.1	59.2	0.35	
Loess-like loam, town of Rostov (non-subsiding)	61.1	35.5	0.72	
Loess-like loam, valley of the Baksan river (non-subsiding)	40.1	21.6	0.85	
Red-brown clay	56.9	29.0	0.97	0.97
Maikop clay	72.0	24.6	1.93	2.13
Do	53.3	19.0	2.33	

The data on the relationship between the degree of dispersion of the ground and the nature of the preparatory procedure make it possible also to revise the arguments in favour of the laminar shape of clayey particles.

In this connexion the results of the experiments of D. P. Krynin ([6]) are considered as fully persuasive; they have been recognized and highly appreciated in the papers of K. Terzaghi ([8]), N. V. Poliakov ([7]) and others.

As known, D. P. Krynin's experiments consisted essentially in the following: a dry powdered clayey ground was introduced into glass tubes, and observations were made of the capillary rise of the water with a vertical and an inclined position of the tubes. It was found that the interface between the ground which had darkened owing to moistening and the ground which was left dry, was normal to the walls of the tubes, irrespective of their position. In experiments carried out with sand this surface had a horizontal position. Such a difference between the position of the zone of capillary saturation in clays and in sands was referred by the author to the fact that because of their laminar shape the clayey particles were assuming a horizontal position.

However, the data on the influence of the nature of the preparatory treatment upon the degree of dispersion of the soil-grounds clearly demonstrate that as a result of a preliminary grinding of clays in a dry condition it is not possible to attain their complete desaggregation, and hence the experiments were carried out not on clayey particles, but on their aggregates which certainly are of no laminar shape.

Received
28. VIII. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

PLANT PHYSIOLOGY

LATEX SYSTEM IN KOK-SAGHYZ AS A SYSTEM FOR CONTROLLING WATER ECONOMY OF THE PLANT

By A. A. NICHIPOROVICH

(Communicated by A. N. Bach, Member of the Academy, 10.III.1943)

Among many other functions that are being attributed to the laticiferous vessels in plants, some writers ([1–3]) believe them to control the water economy, serving as a magazine for storing water. There are, however, others ([4–6]) who refute the probability of such an interpretation. The present author was brought to adhere to the latter opinion ([7]) on the ground of the following considerations: under favourable conditions fresh roots, say, of kok-saghyz which is a plant endowed with a well-developed system of laticiferous vessels, at best contain 2—2.5 per cent of rubber dispersed in the latex. The concentration of the latex is 30—40 per cent.

Thus, the weight of water contained in the latex makes up 5—7.5 per cent to the total weight of raw roots, or about 6.7—10 per cent to the total weight of water contained in the root. If even we were to assume the latex water as being stable bound, its amount is nevertheless so insignificant that it cannot possibly play any important part as a reserve store in the general balance of moisture of the plant.

As to the rest of plants, most of them contain a still smaller quantity of latex and have a still lower water content in the latter.

This circumstance, however, does not make it impossible to regard laticiferous vessels as a most important factor controlling the plant's water economy, though not as a reservoir for storing stably preserved moisture, but rather as a system of canals that serve to interconnect water adsorbing and evaporating organs.

The following facts speak in favour of this opinion:

1. If for some reason the laticiferous vessels become poor in latex, they develop a great suction pressure and begin intensely to suck in water from the adjoining parenchymatous cells. It is upon this phenomenon made use of in a due way, that the system of tapping of rubber-yielding plants and, in particular, of *Hevea* is based. Excessive tappings provoke in this plant a bark disease named the «brown bast». According to Frey-Wyssling ([8]), this disease is due to a pathological dehydration of the parenchymatous cells, caused by an increased absorption of water by laticiferous vessels.

2. The laticiferous vessels form a system of uninterrupted canals interconnecting the tissues of various organs, both water-absorbing and conducting as well as evaporating. The diameters of these canals are usually rather large: thus, in *Hevea* they are on the average 26 μ across ([8]), in kok-saghyz, according to our measurements, they attain 15—35 μ, in representatives of the family *Sapotaceae*, up to 50 μ ([9]).

The large diameters of the laticiferous vessels greatly facilitate the migration of liquids along them, in case favourable conditions are created.

Aside from the laticiferous vessels being artificially opened, migration of liquids along them may be due to local water losses by the parenchymatous cells within a definite zone of the plant. In this case part of the water must be absorbed from the adjoining zone of the laticiferous vessels, while water will migrate towards this zone from other parts of the laticiferous vessels. In another zone the equilibrium of the suction pressure will therefore be disturbed in favour of the laticiferous vessels, and now it is the laticiferous vessels that will absorb water from the neighbouring cells. Thus, for example, if there are created severe disturbances of water equilibrium in the leaves, the laticiferous vessels may serve to facilitate the supply of water from other organs. And inversely, if water is supplied in insufficient amounts from the soil and the cells of the storing tissues of the axial organs become poor in water, then an impulse may be transmitted through the laticiferous vessels to reduce transpiration by the leaves. The relation between the water balance of the plant and the water regime in the laticiferous vessels was established by numerous investigations([3], [5], [10]). We do not know, however, such studies that would elucidate the question as to how far the laticiferous vessels may participate in the control of the plant's transpiration.

In order to clear this question we have carried out the following experiments with kok-saghyz.

In pots with well moistened soil the roots of the kok-saghyz plants were laid bare about 4—5 cm deep. A total of nine plants were prepared for the experiment. The roots of three of them were subjected to no additional treatment. In others incisions were made with a razor on the bark of their roots, which caused the latex to flow out, but did not injure the wood. In one case (second lot) the incisions were practised every 10 minutes during one hour (from 10 to 11 a, m), after which they were stopped. The roots of the third lot were subjected to a similar operation, the only difference being that the incisions were renewed every 20 minutes during 3 hours (from 10 a. m. to 1 p. m.). The intensity of transpiration in all the experimental plants was recorded every hour by the cobalt-chloride test, in our modification ([11]).

The results of our observations are tabulated below.

Table 1

Lot of plants	Mean relative indices of transpiration intensity related to hour									
	9—10	10—11	11—12	12—13	13—14	14—15	15—16	16—17	17—18	18—19
Control	100	139	205	324	374	350	398	297	148	105
2nd lot	100	87	94	189	225	304	312	248	114	94
3rd lot	100	94	103	84	120	154	235	217	175	102

As may be seen from the data tabulated above, the cuts made on the bark of the root in order to produce outflow of the latex, considerably reduce the intensity of transpiration. Some 3 — 4 hours after tapping is over, when the initial equilibrium between the suction pressure of the laticiferous vessels and that of the cells of the mesophyll of the leaves is likely to be restored, the intensity of transpiration is, however, restored as well. Such an experiment may, however, be open to criticism, its results being dependent not only on disturbances of equilibrium between the suction pressure of the laticiferous vessels and the parenchymatous cells, but also on the traumas inflicted to the water-sucking and water-conveying organs, the roots. In order to avoid this argument, another experiment was carried out, in which part of the latex was extracted from the laticiferous vessels through overground organs, viz. the peduncle. During the

period of mass flowering, the succulent peduncles excrete at the places of cutting a large amount of latex. In an earlier work it has been shown that the laticiferous vessels of kok-saghyz form a complete system connecting by a dense network of canals all the organs of the plant. Thus, by extracting latex from the peduncles, we reduce the turgor and increase the suction power in the laticiferous vessels of roots and leaves.

The experiment involved eight plants taken from a well watered plot at the stage of mass flowering. Each of them bore up to 20—30 peduncles at the stage of budding, blossoming and, partly, of early seed ripening. Four plants were kept as controls. In four others, the peduncles were cut off directly under the heads. As soon as large drops of latex had appeared on the cuts, the procedure was reiterated 0.4—0.5 cm below the first cuts. After a few minutes the operation was repeated once more; and again, until the outflux of latex ceased altogether, or, at least, diminished considerably.

By this moment the results of the operation could already be evaluated visually: while the leaves of the control plants preserved their turgor, those of the experimental plants have appreciably lost it and showed various degrees of wilting.

Determination of the intensity of transpiration by the cobalt-chloride test gave the following results:

Table 2

Lot of plants	Intensity of transpiration in relative indices					
	prior to cutting	upon cutting	next day	with control indices being 100		
	I	II	III	I	II	III
Controls	100	123	115	100	100	100
Experiments	100	32	193	117	30.5	196

The experiment makes it quite evident that the turgor regime of the laticiferous vessels is an important factor controlling the distribution of water throughout the tissues and organs of the plant, and regulating their transpiration.

It should be kept in mind that the presence of well-developed latex systems is inherent mostly in herbacious plants of the xerophyte type, or in high-grown trees and long-stem tropical lianas which not infrequently shed their leaves during the dry eason. It is well known that even in the case of abundant precipitations arborial plants of these types often show a clear-cut evidence of their xeromorphism in the form of thick, skinny, lustrous leaves with a well-developed vessel system, etc.

All these characters testify to the difficulties these plants suffer in their water economy.

It is of interest to note that the presence of laticiferous vessels is typical of many plants growing in such regions as are characterized by a sharply expressed periodicity and alternation of humid and droughty periods. As a response to such conditions many of these plants developed in the course of evolution into a type of perennial ephemeroids, vegetating only during the humid period of the spring and summer, and passing into quiescence as soon as the drought season sets in. Among such plants should be classed also our kok-saghyz, krym-saghyz, tau-saghyz, and many others.

It is but natural to assume that the laticiferous vessels play an important rôle in the life-activity of these plants. During temporal water deficiency or if it is supplied to the roots in insufficient quantities, the laticiferous vessels may

serve as a supplementary system of controlling the process of water absorption by the roots and its evaporation by the leaves.

If the soil shows a prolonged and stable decrease of humidity, and the most important reserve tissues of the roots (parenchyma) also begin to grow poor in water, then the laticiferous vessels may act as sensitive and efficient organs, conveying to the leaves stimuli that will at due time impel them to pass into a state of quiescence.

Under these conditions the part of the laticiferous vessels as a supplementary system of controlling the plant's water economy assumes a rather important, though by no means unique aspect.

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Received
12. IV. 1943.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLII, № 4

MICROBIOLOGY

PURIFICATION AND CONCENTRATION OF INFLUENZA VIRUS

By V. I. TOVARNIZKY and O. M. CHALKINA

(Communicated by L. A. Orbeli, Member of the Academy, 24.XII.1943)

Studies concerned with the application of adsorption methods to purification and concentration of enzymes are universally known. But the value of these methods is especially high when applied to unstable animal and human viruses, both owing to their freedom of any injurious effect of chemical agents, and on account of their simplicity. Our aim was to choose such an adsorbing agent that would adsorb the influenza virus without, however, adsorbing other protein substances of the lung tissue. Our choice fell upon the colloidal gypsum, used at the moment of its falling out of solution.

Suspension of lung tissue of a due concentration was prepared as usual on water saturated with gypsum. The formation of a colloidal precipitate is brought about by adding to this suspension 30 per cent of ethyl alcohol by volume. The precipitate that falls out is separated t gether with the virus adsorbed by centrifugation, and the supernatent fluid which contains ballast proteins is poured out. In order to elute the virus it is sufficient to treat the gypsum precipitate with water or some other liquid. Both gypsum water and alcohol are to be used cooled. Adsorption is carried on in a refrigerator for one hour.

In the case of a 2 per cent solubility of gypsum in water, and of a total absorption of the virus, its concentration upon the gypsum increases 400-fold, since after the gypsum precipitate is dissolved in a volume of water equal to the volume of the suspension originally taken, the titre of the virus, as determined biologically, remains unchanged (Table 1).

Table 1

Dilution	1 : 250	1 : 1250	1 : 6250	1 : 31250	1 : 156250	1 : 781250
Initial virus suspension 1 : 50* .	+++	+++	+++	+++	+++	+−−
Suspension of purified virus . .	+++	+++	++−	+++	++−	++−

Microanalyses have shown that after a single absorption the virus is found to be freed of 75 per cent of foreign proteins (Table 2).

* Sign + signifies that the mouse perished of the virus infection, sign −, that the mouse survived.

Table 2

Fraction	Protein contents	
	in mg	in per cent
Initial suspension of the virus 1 : 100	126	100
Precipitate separated by centrifuging	94	75
Suspension of purified virus	32	25

But the method permits of a twofold purification of the virus, as well. This consists in that upon the dissolution of the gypsum adsorbate in water, it is made to precipitate again with alcohol, and all the procedures are repeated once more. After such a reiterated purification a preparation of a high grade of purity is obtained (93 per cent), its activity being not below that of the initial virus (Tables 3 and 4).

Table 3

Fraction	Protein contents	
	in mg	in per cent
Initial suspension of the virus 1 : 20	854	100
Suspension of a virus after twofold purification	59	7

Table 4

Dilution	1 : 100	1 : 500	1 : 2500	1 : 12500	1 : 62500	1 : 312500	1 : 1562500	1 : 7812500
Initial suspension of the virus 1 : 20	+++	+++	+++	++−	+++	+++	++−	+−−
Suspension of a virus after twofold purification	+++	+++	+++	+++	+++	+++	++−	++−

Experiments carried out in order to check the theory of the gypsum method for purification of viruses have shown that the selective adsorption of the virus by gypsum is associated with the adsorption of elementary bodies at the moment they are dehydrated with alcohol, rather than with some peculiar properties of the salt. The elution of the virus may take place in two ways: either by dissolution of the gypsum precipitate, attended by a transfer of the elementary bodies to a free state, or without dissolution of the gypsum precipitate, by way of splitting off elementary bodies from the adsorbing agent because of their hydration.

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Received 17. VII. 1943.

Prix $ 0.50